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Supporting Information

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Supporting Information

Phosphonium and Borate-Bridged Zwitterionic Ladder Stilbene and Its Extended Analogues

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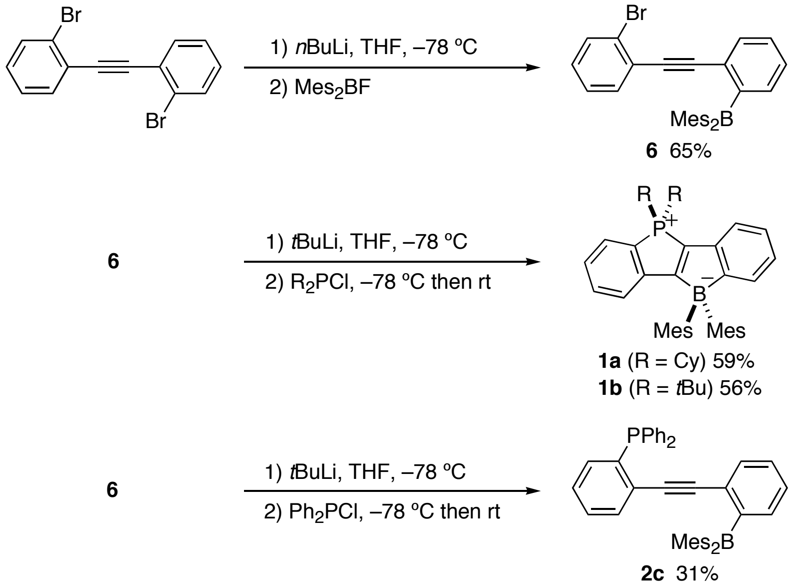
Contents

1. Experimental detail

General. Melting points (mp) were determined with a Stanford Research Systems OptiMelt MPA100 instrument. ^{1}H and ^{13}C NMR spectra were measured with a JEOL A-400 or AL-400 (400 MHz for ^{1}H, and 100 MHz for ^{13}C) spectrometer in $CDCl_3$ or C_6D_6. Chemical shifts are reported in δ ppm using $CHCl_3$ (7.26 ppm) or C_6HD_5 (7.15 ppm) for ^{1}H NMR and using $CDCl_3$ (77.00 ppm) or C_6D_6 (128.06 ppm) for ^{13}C NMR as an internal standard. ^{11}B NMR spectra were recorded with a JEOL A-400 or AL-400 (128 MHz for ^{11}B) spectrometer, and ^{31}P NMR spectra with a JEOL AL-400 (162 MHz for ^{31}P) spectrometer using using $BF_3{\cdot}OEt_2$ (0.0 ppm) and H_3PO_4 (0.0 ppm) as an external standard, respectively. Mass spectra were measured with a JEOL JMS700. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of Silica Gel 60 F-254 (Merck). Column chromatography was performed using neutral silica gel PSQ 60B or PSQ 100B (Fuji Silysia Chemical). Bis(2-bromophenyl)acetylene,[1] 1,4-diethynyl-2,5- bis(dimesitylboryl)benzene,[2] 1-Bromo-2-(trimethylsilyl)ethynylbenzene,[1] and bis(3-bromo- 2-thienyl)acetylene[3] were prepared according to the literatures. All reactions were performed under an argon atmosphere, unless stated otherwise. Dry THF was purchased from Kanto Chemicals.

Scheme S1



(2-Bromophenyl){2′-(dimesitylboryl)phenyl}acetylene (6). To a solution of bis(2-bromophenyl)acetylene[1] (3.36 g, 10.0 mmol) in dry THF (50 mL) was added a hexane solution of *n*BuLi (1.60 M, 6.25 mL, 10.0 mmol) dropwise over 5 min at –78 °C. After stirring for 1 h, Mes_2BF (2.95 g, 11.0 mmol) in dry THF (25 mL) was added dropwise over 3 min at the same temperature. The mixture was allowed to warm to room temperature with stirring over 6 h. After the reaction was quenched with 5% NH_4Cl aq., the resulting aqueous layer was extracted with ether (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual brown oil was subjected to column chromatography (silica gel (PSQ 100B), hexane/AcOEt (50/1) as eluent) to afford 3.30 g ($R_f = 0.20$, 6.53 mmol, 65% yield) of **6** as white solids. Mp: 164–165 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 12H), 2.24 (s, 6H), 6.74–6.76 (m, overlapped, 1H), 6.76 (s, overlapped, 4H), 7.08 (dt, J = 7.6 Hz, J = 1.7 Hz, 1H), 7.11 (dt, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.27–7.33 (m, 2H), 7.41 (dt, J = 7.5 Hz, J = 2.2 Hz, 1H), 7.50 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.20 (CH_3), 23.20 (CH_3), 91.02 (C), 94.58 (C), 125.31 (C), 125.59 (C), 128.25 (C), 126.34 (CH), 126.98 (C), 128.16 (CH), 128.27 (CH), 128.82 (CH), 130.33 (CH), 133.08 (CH), 133.44 (CH), 134.60 (CH), 138.98 (C), 140.86 (C), 142.74 (C), 149.88 (C). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 75.72. MS (FAB): m/z (relative intensity) 503.2 (36), 504.2 (94), 505.2 (79), 506.2 (100), 507.2 (44), 508.2 (10). HRMS (FAB): m/z 504.1631 (M^+), calcd. for $C_{32}H_{30}BBr$: 504.1624.

Compound 1a. To a solution of **6** (101 mg, 0.200 mmol) in dry THF (2.0 mL) was added a pentane solution of *t*BuLi (1.58 M, 0.253 mL, 0.400 mmol) dropwise over 2 min at –78 ºC. After stirring for 1 h, Cy_2PCl (46.5 mg, 0.200 mmol) was added dropwise over 1 min at the same temperature. The mixture was allowed to warm to room temperature with stirring over 10 h. Then, the mixture was concentrated under reduced pressure. Toluene (10 mL) was added into the residue, and insoluble salts were removed by filtration. The filtrate was evaporated and successively subjected to column chromatography (silica gel (PSQ 60B), toluene as eluent) to afford 77.7 mg ($R_f = 0.41$, 0.117 mmol, 59% yield) of **1a** as yellow solids. Mp: > 280 °C (decomposition without melting is observed at 280 ºC in sealed tube filled with Ar). ^1H NMR (400 MHz, $CDCl_3$): δ 1.12–1.21 (m, 2H), 1.25–1.37 (m, 4H), 1.41–1.45 (m, overlapped with the peak of H_2O, 4H), 1.74 (d, J = 12.4 Hz, 2H), 1.78–1.88 (m, 6H), 1.97 (s, 12H), 2.06–2.15 (m, overlapped, 2H), 2.14 (s, overlapped, 6H), 2.58–2.68 (m, 2H), 6.58 (s, 4H), 6.96 (t, J = 7.3 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.3 Hz, 1H), 7.15–7.20 (m, 1H), 7.44 (t, J = 8.3 Hz, overlapped, 1H), 7.46 (t, J = 8.5 Hz, overlapped, 1H), 7.63 (d, J = 6.8 Hz, 1H), 8.02 (dd, J = 7.9 Hz, J = 2.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 20.74 (s, CH_3), 25.19 (d, CH_2, $^3J_{CP}$ = 1.7 Hz), 26.07 (s, CH_3), 26.27 (overlapped, CH_2), 26.30 (overlapped, CH_2), 26.43 (d, CH_2, $^2J_{CP}$ = 2.5 Hz), 26.74 (d, CH_2, $^2J_{CP}$ = 2.5 Hz), 32.01 (d, CH, $^1J_{CP}$ = 41.4 Hz), 119.29 (s, CH), 123.23 (s, CH), 123.28 (d, C, $^1J_{CP}$ = 89.4 Hz), 124.29 (d, C, $^1J_{CP}$ = 62.9 Hz), 125.12 (s, CH), 126.19 (d, CH, $^3J_{CP}$ = 9.9 Hz), 128.68 (s, overlapped, CH), 128.76 (overlapped, CH), 129.05 (d, CH, $^3J_{CP}$ = 10.8 Hz), 131.34 (s, C), 132.36 (s, CH), 134.94 (d, CH, $^2J_{CP}$ = 1.7 Hz), 140.87 (s, C), 142.94 (d, C, $^2J_{CP}$ = 18.2 Hz), 152.51 (d, C, $^2J_{CP}$

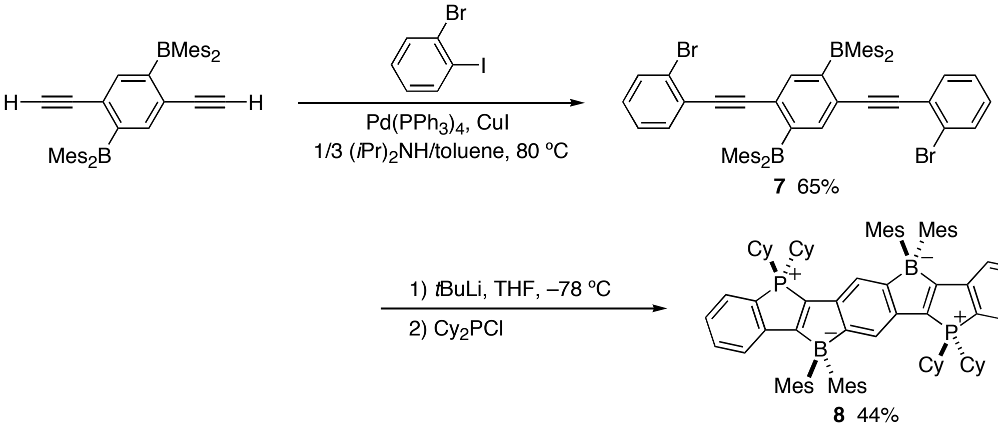
= 22.3 Hz), signals of three carbons bound to boron were not observed. ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ –4.94. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 31.85. HRMS (FAB): *m/z* 622.3892 (M^+), calcd. for $C_{44}H_{52}BP$: 622.3900.

Compound 1b. This compound was prepared in 56% yield in the similar manner as described for **1a**. Mp: > 250 °C (Decomposition without melting is observed at 250 ºC in sealed tube filled with Ar). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.50 (d, J = 15.9 Hz, 18H), 1.97 (s, 12H), 2.13 (s, 6H), 6.57 (s, 4H), 6.95 (t, J = 7.3 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H), 7.17–7.22 (m, 1H), 7.26–7.28 (overlapped with the peak of residual proton of CDCl$_3$), 7.47 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 8.13 (dd, J = 7.6 Hz, J = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 20.72 (s, *C*H$_3$), 26.25 (s, *C*H$_3$), 28.06 (s, *C*H$_3$), 35.98 (d, *C*, $^{1}J_{CP}$ = 33.1 Hz), 120.44 (s, *C*H), 123.14 (s, *C*H), 124.86 (s, *C*H), 125.47 (d, *C*, $^{1}J_{CP}$ = 97.7 Hz), 126.07 (d, *C*H, $^{3}J_{CP}$ = 9.9 Hz), 126.17 (d, *C*, $^{1}J_{CP}$ = 57.1 Hz), 128.73 (s, *C*H), 128.97 (d, *C*H, $^{3}J_{CP}$ = 8.3 Hz), 129.23 (d, *C*H, $^{3}J_{CP}$ = 9.1 Hz), 131.25 (s, *C*), 132.51 (s, *C*H), 134.42 (d, *C*H, $^{2}J_{CP}$ = 2.5 Hz), 140.75 (s, *C*), 143.15 (d, *C*, $^{2}J_{CP}$ = 17.4 Hz), 152.06 (d, *C*, $^{2}J_{CP}$ = 19.9 Hz), signals of three carbons bound to boron were not observed. ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ –5.21. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 47.82. HRMS (FAB): *m/z* 570.3570 (M^+), calcd. for $C_{40}H_{48}BP$: 570.3587.

{2-(Dimesitylboryl)phenyl}{2′-(diphenylphosphino)phenyl}acetylene (2c). To a solution of **6** (505 mg, 1.0 mmol) in dry THF (10 mL) was added a pentane solution of *t*BuLi (1.50 M, 1.33 mL, 2.00 mmol) dropwise over 3 min at –78 ºC. After stirring for 1 h, Ph$_2$PCl (243 mg, 2.10 mmol) was added dropwise over 1 min at the same temperature. The mixture was allowed to warm to room temperature with stirring over 8 h. After the mixture was concentrated under reduced pressure, toluene was added, and insoluble salts were removed by filtration. The filtrate was passed through a plug of silica gel (PSQ 100B) and washed with toluene. The crude product was then washed with hexane to give 188 mg (0.308 mmol, 31% yield) of **2c** as white solids. Mp: 141–142 ºC (sealed tube filled with Ar). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.97 (s, 12H), 2.26 (s, 6H), 6.65–6.67 (m, 1H), 6.70–6.72 (m, 1H), 6.75 (s, 4H), 7.08–7.22 (m, 5H), 7.26–7.32 (overlapped with the peak of residual proton of CDCl$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 21.21 (s, *C*H$_3$), 23.12 (s, *C*H$_3$), 91.77 (d, *C*, $^{3}J_{CP}$ = 8.3 Hz), 96.99 (d, *C*, $^{4}J_{CP}$ = 2.5 Hz), 127.22 (s, *C*), 127.57 (s, *C*H), 127.66 (d, *C*H, $^{2}J_{CP}$ = 8.3 Hz), 127.89 (s, *C*), 128.20 (s, *C*H), 128.39 (d, *C*H, $^{2}J_{CP}$ = 6.6 Hz), 128.60 (s, *C*H), 130.08 (s, *C*H), 131.83 (s, *C*H), 132.50 (d, *C*H, $^{3}J_{CP}$ = 3.3 Hz), 132.97 (s, *C*H), 133.92 (s, *C*H), 134.12 (s, *C*H), 134.30 (s, *C*H), 136.71 (d, *C*, $^{1}J_{CP}$ = 10.8 Hz), 138.76 (s, *C*), 140.34 (d, *C*, $^{1}J_{CP}$ = 12.4 Hz), 142.76 (br s, *C*), 149.27 (br s, *C*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ 73.98. ^{31}P{^{1}H} NMR

(162 MHz, $CDCl_3$): δ –8.14. HRMS (FAB): *m/z* 610.2949 (M^+), calcd. for $C_{40}H_{48}BP$: 610.2961.

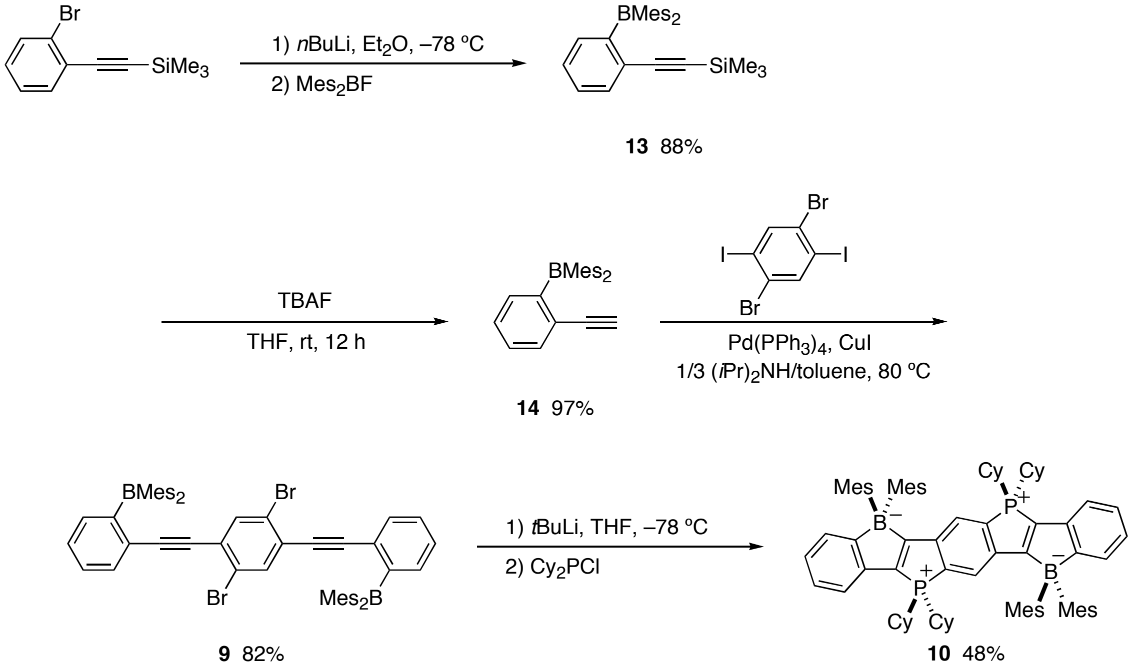
Scheme S2



1,4-Bis(2-bromophenylethynyl)-2,5-bis(dimesitylboryl)benzene (7). A (iPr)$_2$NEt/toluene (1/3) mixed solvent was degassed with Ar bubbling prior to use. To a solution of a mixture of 2-bromoiodobenzene (1.24 g, 4.40 mmol), $Pd(PPh_3)_4$ (49.8 mg, 40.0 μmol), and CuI (15.2 mg, 80.0 μmol) in a (iPr)$_2$NH/toluene (1/3) (80 mL) mixed solvent was added a solution of 1,4-diethynyl-2,5-bis(dimesitylboryl)benzene[2] (1.25 g, 2.00 mmol) in a (iPr)$_2$NEt/toluene (1/3) (40 mL) mixed solvent at room temperature. The reaction mixture was stirred at 80 °C for 24 h. After the reaction was quenched with 5% NH_4Cl aq., the resulting aqueous layer was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual mixture was subjected to column chromatography (silica gel (PSQ 100B), toluene as eluent) to afford 1.56 g (R_f = 0.95, 1.67 mmol, 65% yield) of **7** as yellow solids. Mp: > 280 °C (Decomposition without melting is observed at 280 °C in sealed tube filled with Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 24H), 2.22 (s, 12H), 6.73 (s, 8H), 6.77 (d, J = 7.6 Hz, 2H), 7.03–7.11 (m, 4H), 7.46 (d, J = 7.8 Hz, 2H), 7.53 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.20 (CH$_3$), 23.34 (CH$_3$), 92.64 (C), 94.54 (C), 125.35 (C), 126.14 (C), 126.28 (CH), 128.33 (CH), 128.92 (CH), 131.94 (CH), 133.32 (CH), 138.37 (CH), 139.26 (C), 140.87 (C), 142.40 (C), 151.65 (C). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 76.42. MS (FAB): *m/z* (relative intensity) 928.3 (30), 929.3 (36), 930.3 (68), 931.3 (76), 932.3 (100), 933.3 (99), 934.3 (72), 935.3 (58), 936.3 (30). HRMS (FAB): *m/z* 930.2795 (M^+), calcd. for $C_{58}H_{54}B_2Br_2$: 930.2778.

Compound 8. To a solution of **7** (93.2 mg, 0.100 mmol) in dry THF (8 mL) was added a pentane solution of *t*BuLi (1.58 M, 0.253 mL, 0.400 mmol) dropwise over 2 min at –78 ºC. After stirring for 1.5 h, Cy_2PCl (51.2 mg, 0.220 mmol) was added dropwise over 1 min at the same temperature. The mixture was gradually warmed to room temperature with stirring over 12 h. After the mixture was concentrated under reduced pressure, toluene was added, and insoluble salts were removed by filtration. After evaporation of solvents, the resulting orange solids were subjected to column chromatography (silica gel (PSQ 100B), toluene as eluent) to afford 51.4 mg (R_f = 0.45, 0.0440 mmol, 44% yield) of **8** as orange solids. Mp: > 300 ºC (sealed tube filled with Ar). ^{1}H NMR (C_6D_6): δ 0.75–1.13 (m, 16H), 1.23–1.45 (m, 16H), 1.58 (d, J = 11.2 Hz, 4H), 1.92–1.99 (m, 4H), 2.15–2.26 (m, overlapped, 4H), 2.30 (s, overlapped, 12H), 2.59 (s, 24H), 6.61–6.65 (m, 2H), 6.71 (t, J = 7.4 Hz, 2H), 6.95 (s, 8H), 7.09–7.15 (overlapped with the peak of residual proton of C_6D_6), 7.75 (d, J = 1.7 Hz, 2H), 8.33 (dd, J = 8.0 Hz, J = 2.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 21.22 (s, CH$_3$), 25.33 (s, CH$_2$), 26.13 (d, CH$_2$, $^2J_{CP}$ = 3.3 Hz), 26.44 (s, CH$_2$), 26.57 (s, CH$_2$), 26.70 (d, CH$_2$, $^2J_{CP}$ = 1.7 Hz), 27.29 (s, CH$_3$), 31.98 (d, CH, $^1J_{CP}$ = 41.4 Hz), 124.00 (d, C, $^1J_{CP}$ = 87.7 Hz), 125.15 (d, CH, $^3J_{CP}$ = 10.8 Hz), 125.30 (s, CH), 126.97 (d, C, $^1J_{CP}$ = 61.2 Hz), 128.22 (d, CH, $^3J_{CP}$ = 8.3 Hz), 128.75 (d, CH, $^3J_{CP}$ = 9.9 Hz), 129.75 (s, CH), 131.11 (s, C), 134.83 (s, CH), 141.12 (br s, C), 142.08 (d, C, $^2J_{CP}$ = 18.2 Hz), 154.13 (d, C, $^2J_{CP}$ = 22.3 Hz), signals of three carbons bound to boron were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ –4.46. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 30.69. HRMS (FAB): *m/z* 1166.7312 (M^+), calcd. for $C_{82}H_{98}B_2P_2$: 1166.7330.

Scheme S3



1-Dimesitylboryl-2-(trimethylsilyl)ethynylbenzene (13). To a solution of 1-Bromo-2-(trimethylsilyl)ethynylbenzene[1] (4.98 g, 19.7 mmol) in dry Et_2O (100 mL) was added a hexane solution of *n*BuLi (1.50 M, 13.1 mL, 19.7 mmol) dropwise over 5 min at –78 ºC. After stirring for 1 h, Mes_2BF (5.82 g, 21.7 mmol) in dry Et_2O (50 mL) was added dropwise over 5 min at the same temperature. The mixture was allowed to warm to room temperature with stirring over 6 h. After the reaction was quenched with 5% NH_4Cl aq., the resulting aqueous layer was extracted with ether (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual yellow oil was subjected to column chromatography (silica gel (PSQ 100B), hexane/AcOEt (100/1) as eluent) to afford 7.36 g ($R_f = 0.35$, 17.4 mmol, 88% yield) of **13** as white solids. Mp: 107–108 °C. ^1H NMR (400 MHz, $CDCl_3$): δ –0.02 (s, 9H), 1.99 (s, 12H), 2.28 (s, 6H), 6.75 (s, 4H), 7.22–7.24 (m, 2H), 7.30–7.34 (m, 1H), 7.48 (d, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ –0.31 (CH_3), 21.26 (CH_3), 23.13 (CH_3), 97.29 (C), 104.82 (C), 126.88 (C), 127.90 (CH), 128.18 (CH), 129.90 (CH), 133.44 (CH), 133.90 (CH), 138.95 (C), 140.78 (C), 142.77 (C), 150.72 (C). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 73.76. HRMS (FAB): *m/z* 422.2599 (M^+), calcd. for $C_{29}H_{35}BSi$: 422.2601.

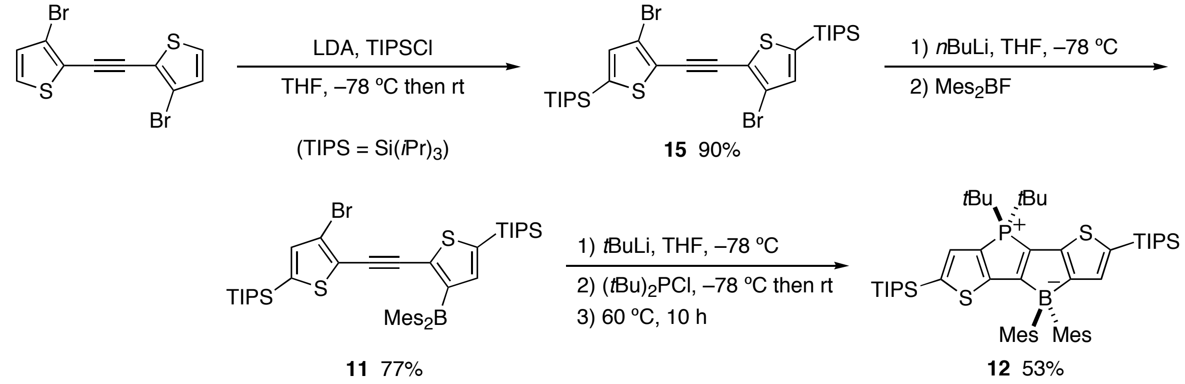
1-Dimesitylboryl-2-ethynylbenzene (14). To a solution of **13** (4.22 g, 10.0 mmol) in THF (50 mL) was added a THF solution of tetrabutylammonium fluoride (TBAF, 1.0 M, 100 mL, 100 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 6 h. After the mixture was concentrated under reduced pressure, water was added into the mixture. The resulting aqueous layer was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual mixture was subjected to column chromatography (silica gel (PSQ 100B), hexane/AcOEt (30/1) as eluent) to afford 3.40 g ($R_f =$ 0.31, 9.71 mmol, 97% yield) of **14** as yellow solids. Mp: 136–137 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 12H), 2.31 (s, 6H), 2.73 (s, 1H), 6.79 (s, 4H), 7.26–7.34 (m, overlapped, 2H), 7.34–7.39 (m, overlapped, 1H), 7.52 (d, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.26 (CH_3), 23.03 (CH_3), 79.86 (CH), 83.18 (C), 125.78 (C), 128.00 (CH), 128.14 (CH), 129.98 (CH), 133.12 (CH), 133.93 (CH), 139.05 (C), 140.81 (C), 142.70 (C), 151.32 (C). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 74.29. HRMS (FAB): *m/z* 350.2198 (M^+), calcd. for $C_{26}H_{27}B$: 350.2206.

1,4-Dibromo-2,5-bis[{2′-(dimesitylboryl)phenyl}ethynyl]benzene (9). A $(iPr)_2NEt$/toluene (1/3) mixed solvent was degassed with Ar bubbling prior to use. To a solution of a mixture of 1,4-Dibromo-2,5-diiodobenzene (1.81 g, 3.71 mmol), $Pd(PPh_3)_4$ (92.3

mg, 74.2 μmol), and CuI (28.2 mg, 148 μmol) in a (iPr)$_2$NH/toluene (1/3) (60 mL) mixed solvent was added a solution of **14** (2.60 g, 7.42 mmol) in a (iPr)$_2$NEt/toluene (1/3) (20 mL) mixed solvent at room temperature. The reaction mixture was stirred at 80 ºC for 4 h. After the reaction was quenched with 5% NH_4Cl aq., the resulting aqueous layer was extracted with toluene. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual mixture was subjected to column chromatography (silica gel (PSQ 100B), toluene as eluent) to afford 2.85 g (R_f = 0.97, 3.06 mmol, 82% yield) of **9** as white solids. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00 (s, 24H), 2.28 (s, 12H), 6.78 (s, overlapped, 8H), 6.80 (s, overlapped, 2H), 7.31 (d, J = 4.1 Hz, 4H), 7.39–7.43 (m, 2H), 7.52 (d, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.33 (CH$_3$), 23.18 (CH$_3$), 89.92 (C), 97.00 (C), 122.87 (C), 125.91 (C), 126.29 (C), 128.37 (CH), 128.61 (CH), 130.38 (CH), 133.13 (CH), 134.63 (CH), 135.78 (CH), 139.24 (C), 140.81 (C), 142.57 (C), 150.01 (C). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 73.52. MS (FAB): m/z (relative intensity) 929.3 (29), 930.3 (60), 931.3 (80), 932.3 (100), 933.3 (83), 934.3 (62), 935.3 (35). HRMS (FAB): m/z 930.2802 (M^+), calcd. for $C_{58}H_{54}B_2Br_2$: 930.2778.

Compound 10. To a solution of **9** (186 mg, 0.200 mmol) in dry THF (16 mL) was added a pentane solution of tBuLi (1.58 M, 0.506 mL, 0.800 mmol) dropwise over 3 min at –78 ºC. After stirring for 1.5 h, Cy_2PCl (102 mg, 0.440 mmol) was added dropwise over 2 min at the same temperature. The mixture was gradually warmed to room temperature with stirring over 12 h. After the mixture was concentrated under reduced pressure, CH_2Cl_2 was added, and insoluble salts were removed by filtration. The filtrate was passed through a plug of silica gel (PSQ 100B) and washed with CH_2Cl_2. The crude product was then washed with toluene to give 112 mg (0.0960 mmol, 48% yield) of **10** as red solids. Mp: > 300 ºC (sealed tube filled with Ar). ^{1}H NMR ($CDCl_3$): δ 1.07–1.20 (m, 4H), 1.21–1.45 (m, 16H), 1.65–1.76 (m, 8H), 1.81–1.90 (m, overlapped, 8H), 1.95 (s, overlapped, 24H), 2.01–2.12 (m, overlapped, 4H), 2.15 (s, overlapped, 12H), 2.49–2.58 (m, 4H), 6.57 (s, 8H), 6.94–7.08 (m, 6H), 7.64 (d, J = 6.8 Hz, 2H), 7.93 (d, J = 8.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 20.81 (s, CH$_3$), 24.99 (s, CH$_2$), 26.17 (s, overlapped, CH$_2$), 26.24 (s, overlapped CH$_3$), 26.30 (s, overlapped, CH$_2$), 26.39 (s, overlapped, CH$_2$), 26.77 (s, CH$_2$), 32.15 (d, CH, $^1J_{CP}$ = 39.7 Hz), 119.79 (s, CH), 125.33 (s, CH), 125.57 (s, CH), 126.43 (d, C, $^1J_{CP}$ = 61.1 Hz), 128.14 (t, CH, J_{CP} = 10.3 Hz), 128.85 (s, CH), 130.60 (d, C, $^1J_{CP}$ = 84.4 Hz), 131.46 (s, C), 132.34 (s, CH), 140.53 (s, C), 142.42 (d, C, $^2J_{CP}$ = 18.2 Hz), 150.27 (dd, C, $^2J_{CP}$ = 33.9 Hz, $^3J_{CP}$ = 10.8 Hz), signals of three carbons bound to boron were not observed. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ –5.04. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.19. HRMS (FAB): m/z 1166.7300 (M^+), calcd. for $C_{82}H_{98}B_2P_2$: 1166.7330.

Scheme S4



Bis(3-bromo-5-triisopropylsilyl-2-thienyl)acetylene (15). To a solution of *n*BuLi in hexane (1.60 M, 11.9 mL, 19.0 mmol) was added dropwise to a solution of (iPr)$_2$NH (2.50 mL, 19.0 mmol) in THF (5 mL) at –78 ºC. After stirring for 1 h, the solution was allowed to warm to 0 ºC over 20 min. The produced solution of lithium diisopropylamide was added dropwise to a solution of bis(3-bromo-2-thienyl)acetylene[3] (3.00 g, 8.62 mmol) and (iPr)$_3$SiCl (4.06 mL, 19.0 mmol) in THF (40 mL) at –78 ºC. After stirring for 1 h, the mixture was allowed to warm to room temperature over 5 h. The mixture was quenched with water, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After concentrating the organic layer, the residual brown solids were subjected to column chromatography (silica gel, hexane/CH_2Cl_2 (8/1) as eluent) to afford 5.10 g (R_f = 0.88, 7.72 mmol, 90% yield) of **15** as pale yellow solids. Mp: 127–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (d, J = 7.3 Hz, 36H), 1.32 (septet, J = 7.3 Hz, 6H), 7.10 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.63 (*C*H), 18.44 (*C*H$_3$), 89.33 (*C*), 117.32 (*C*), 124.96 (*C*), 137.59 (*C*H), 139.17 (*C*). MS (FAB): *m/z* (relative intensity) 658.1 (48), 659.1 (33), 660.1 (100), 661.1 (62), 662.1 (71), 663.1 (42), 664.1 (18). HRMS (FAB): *m/z* 658.0781 (M^+), calcd. for $C_{28}H_{44}Br_2S_2Si_2$: 658.0790.

(3-Bromo-5-triisopropylsilyl-2-thienyl)(5′-triisopropylsilyl-3′-dimesitylboryl-2′-thienyl)-acetylene (11). To a solution of **15** (3.40 g, 5.00 mmol) in dry THF (50 mL) was added a hexane solution of *n*BuLi (1.60 M, 3.13 mL, 5.00 mmol) dropwise over 5 min at –78 ºC. After stirring for 30 min, Mes_2BF (1.47 g, 5.50 mmol) in dry THF (25 mL) was added dropwise over 5 min at the same temperature. The mixture was allowed to warm to room temperature with stirring over 6 h. After the reaction was quenched with 5% NH_4Cl aq., and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual yellow oil was subjected to column chromatography (silica gel, hexane/AcOEt (100/1) as eluent) to afford 3.19 g (R_f = 0.53, 3.89 mmol, 77% yield) of **11** as pale yellow solids. Mp: 114–115ºC.

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.07 (d, *J* = 7.3 Hz, 18H), 1.10 (d, *J* = 7.3 Hz, 18H), 1.27–1.32 (m, 6H), 2.06 (s, 12H), 2.26 (s, 6H), 6.76 (s, 4H), 6.97 (s, 1H), 7.06 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 11.63 (*C*H), 11.73 (*C*H), 18.46 (*C*H$_3$), 18.49 (*C*H$_3$), 21.31 (*C*H$_3$), 23.01 (*C*H$_3$), 88.92 (*C*), 91.68 (*C*), 116.44 (*C*), 125.65 (*C*), 128.25 (*C*H), 136.99 (*C*), 137.28 (*C*H), 137.49 (*C*), 138.13 (*C*), 138.73 (*C*), 140.65 (*C*), 142.10 (*C*), 142.33 (*C*H), 154.49 (*C*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ 68.66. MS (FAB): *m/z* (relative intensity) 827.3 (26), 828.3 (80), 829.3 (68), 830.3 (100), 831.3 (58), 832.3 (29). HRMS (FAB): *m/z* 828.3411 (M^+), calcd. for $C_{46}H_{66}BrS_2Si_2$: 828.3421.

Compound 12. To a solution of **11** (415 mg, 0.500 mmol) in dry THF (10 mL) was added a pentane solution of *t*BuLi (1.58 M, 0.633 mL, 1.00 mmol) dropwise over 3 min at –78 ºC. After stirring for 1 h, (*t*Bu)$_2$PCl (90.3 mg, 0.500 mmol) was added dropwise over 1 min at the same temperature. After gradually warmed to room temperature with stirring over 8 h, the reaction mixture was stirred at 60 ºC for 10 h. After cooled to room temperature, the mixture was concentrated under reduced pressure. Toluene (10 mL) was then added to the mixture, and insoluble salts were removed by filtration. The resulting red solids were subjected to column chromatography (silica gel, toluene as eluent) to afford 236 mg (R_f = 0.38, 0.264 mmol, 53% yield) of **12** as orange solids. Mp: > 170 ºC (Decomposition without melting is observed at 170 ºC in sealed tube filled with Ar). ^{1}H NMR (CDCl$_3$): δ 1.06, 1.07 (d × 2 (overlapped), *J* = 7.2 Hz, 36H), 1.22–1.33 (m, 6H), 1.46 (d, *J* = 16.1 Hz, 18H), 2.00 (br s, 12H), 2.12 (s, 6H), 6.55 (s, 4H), 7.03 (s, 1H), 7.35 (d, *J* = 1.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 11.57 (s, *C*H), 12.14 (s, *C*H), 18.49 (s, *C*H$_3$), 18.83 (s, *C*H$_3$), 20.68 (s, *C*H$_3$), 25.97 (br s, *C*H$_3$), 27.68 (s, *C*H$_3$), 35.32 (d, *C*H$_3$, $^1J_{CP}$ = 35.6 Hz), 121.55 (d, *C*, $^1J_{CP}$ = 88.6 Hz), 124.17 (d, *C*, $^1J_{CP}$ = 67.9 Hz), 128.27 (br s, *C*H), 130.76 (d, *C*H, $^3J_{CP}$ = 14.1 Hz), 131.20 (s, *C*), 132.54 (s, *C*), 138.94 (d, *C*, $^3J_{CP}$ = 9.1 Hz), 140.86 (br s, *C*), 141.59 (s, *C*H), 143.48 (d, *C*, $^2J_{CP}$ = 16.6 Hz), 170.29 (d, *C*, $^2J_{CP}$ = 25.7 Hz), signals of three carbons bound to boron were not observed. ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ –6.47. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 42.78. HRMS (FAB): *m/z* 894.5391 (M^+), calcd. for $C_{54}H_{84}BPS_2Si_2$: 894.5384.

2. NMR spectra

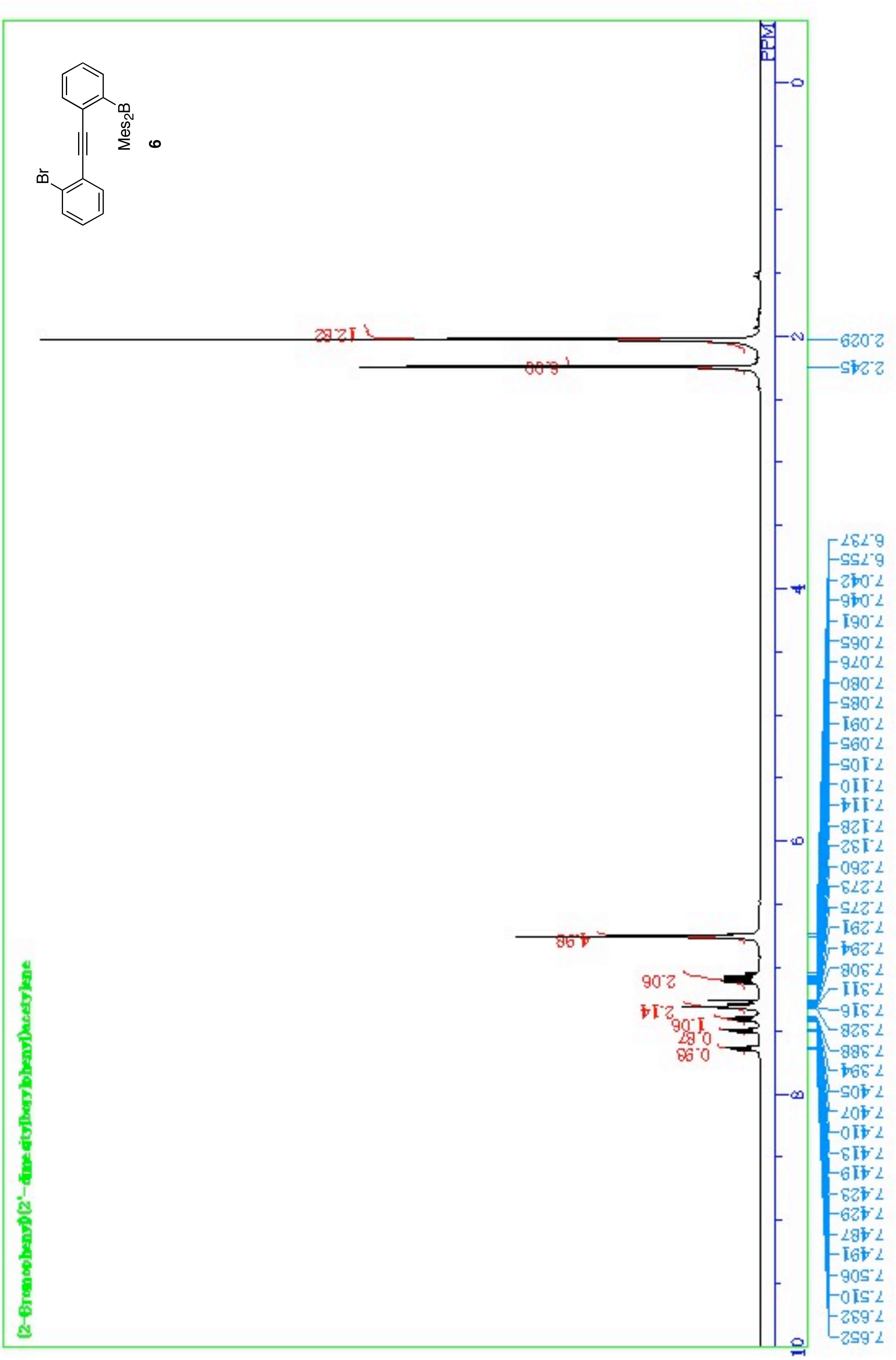


Figure S1. ^{1}H NMR spectrum of **6** (JEOL AL-400, 400 MHz, CDCl$_3$).

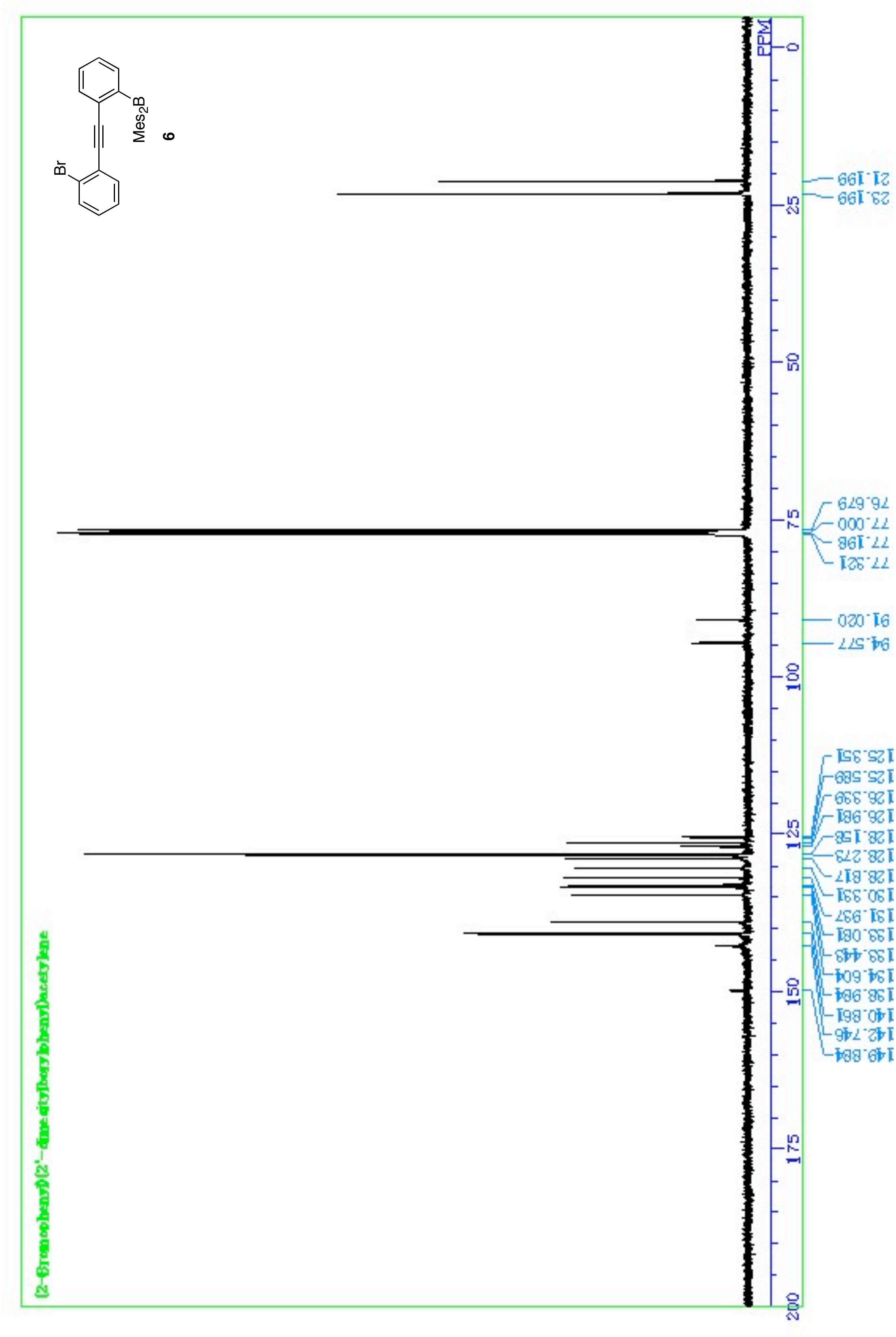


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **6** (JEOL AL-400, 100 MHz, CDCl$_3$).

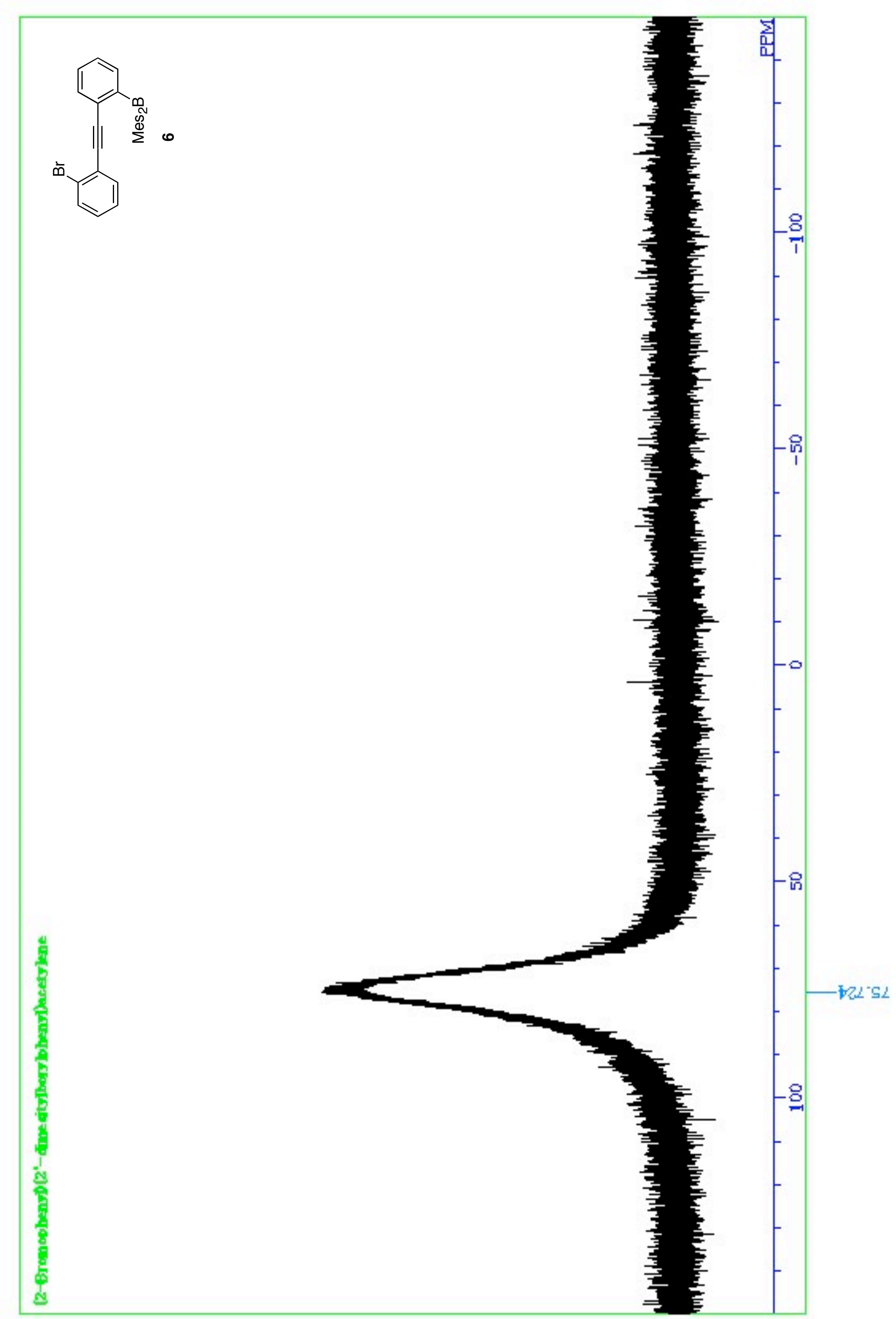


Figure S3. $^{11}B\{^1H\}$ NMR spectrum of **6** (JEOL AL-400, 128 MHz, $CDCl_3$).

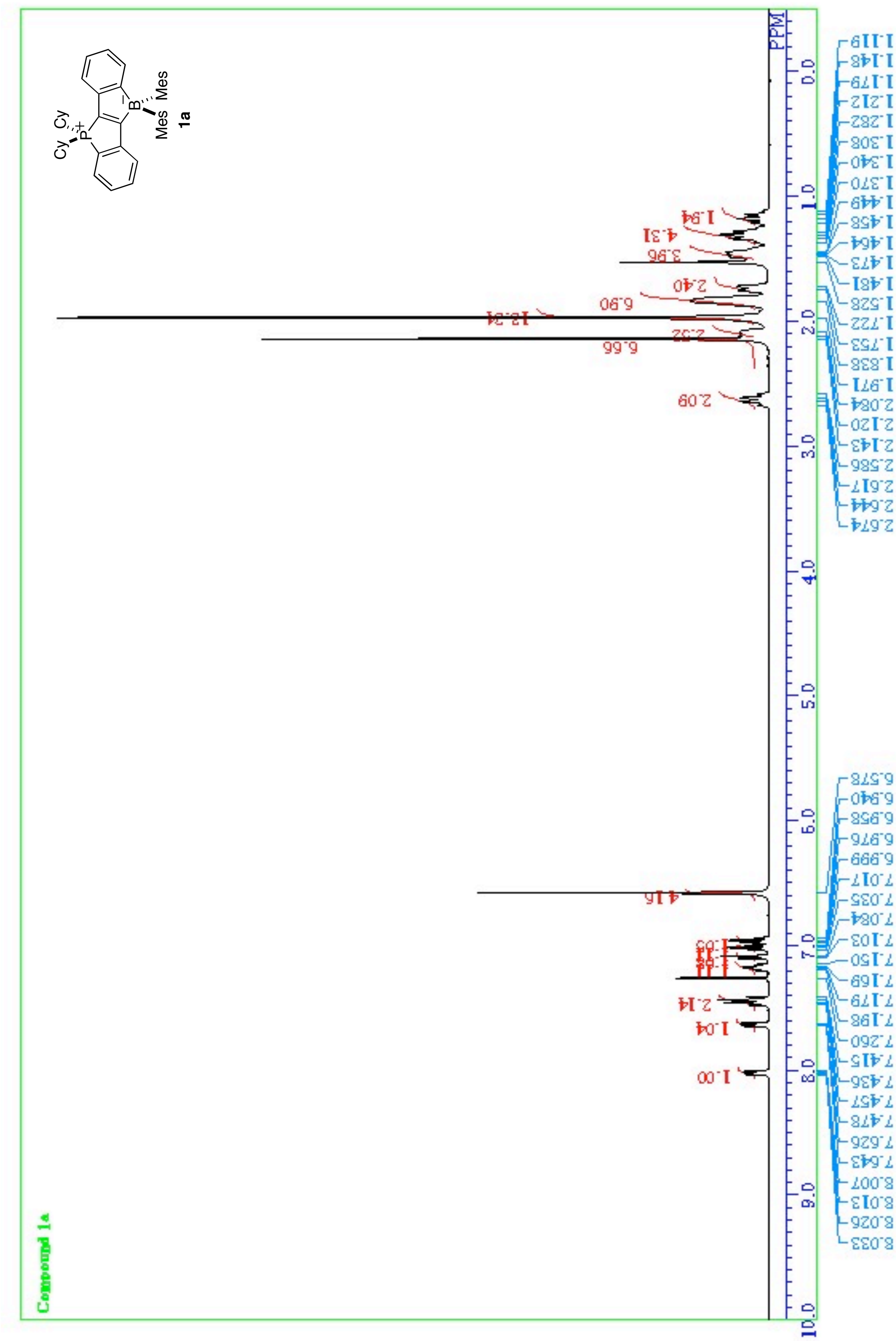


Figure S4. ^{1}H NMR spectrum of **1a** (JEOL AL-400, 400 MHz, CDCl$_3$).

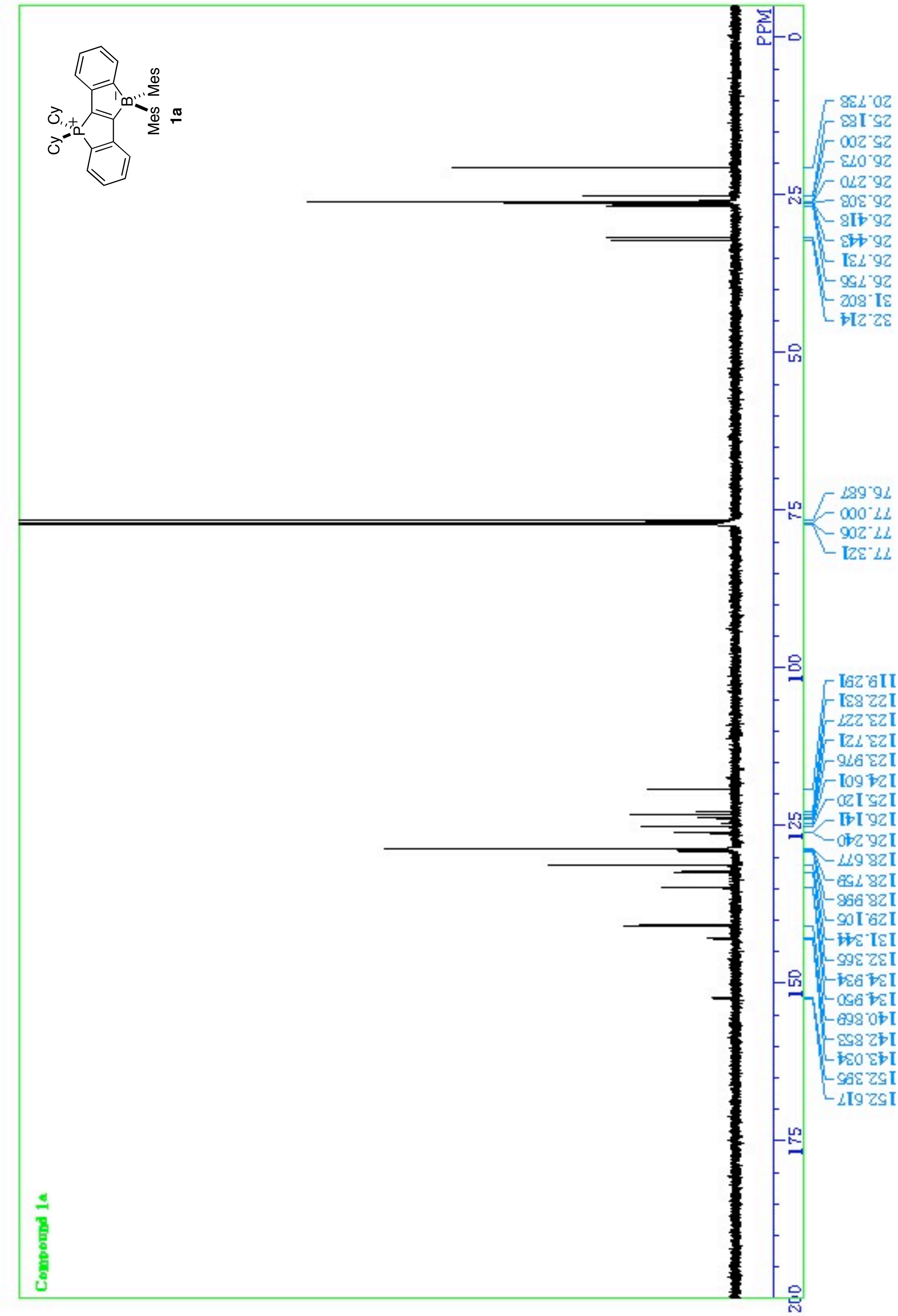


Figure S5. $^{13}C\{^1H\}$ NMR spectrum of **1a** (JEOL AL-400, 100 MHz, $CDCl_3$).

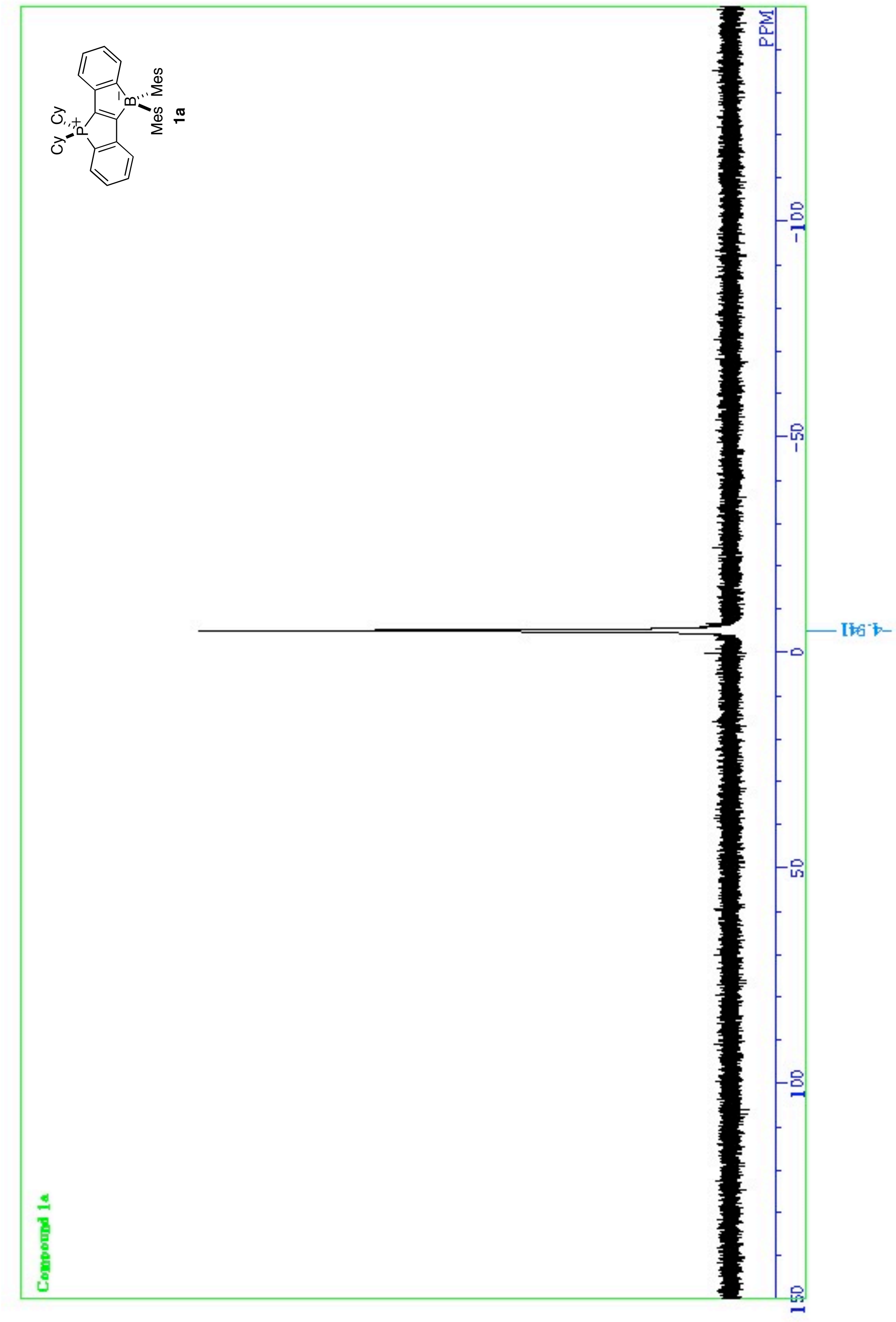


Figure S6. $^{11}B\{^{1}H\}$ NMR spectrum of **1a** (JEOL AL-400, 128 MHz, $CDCl_3$).

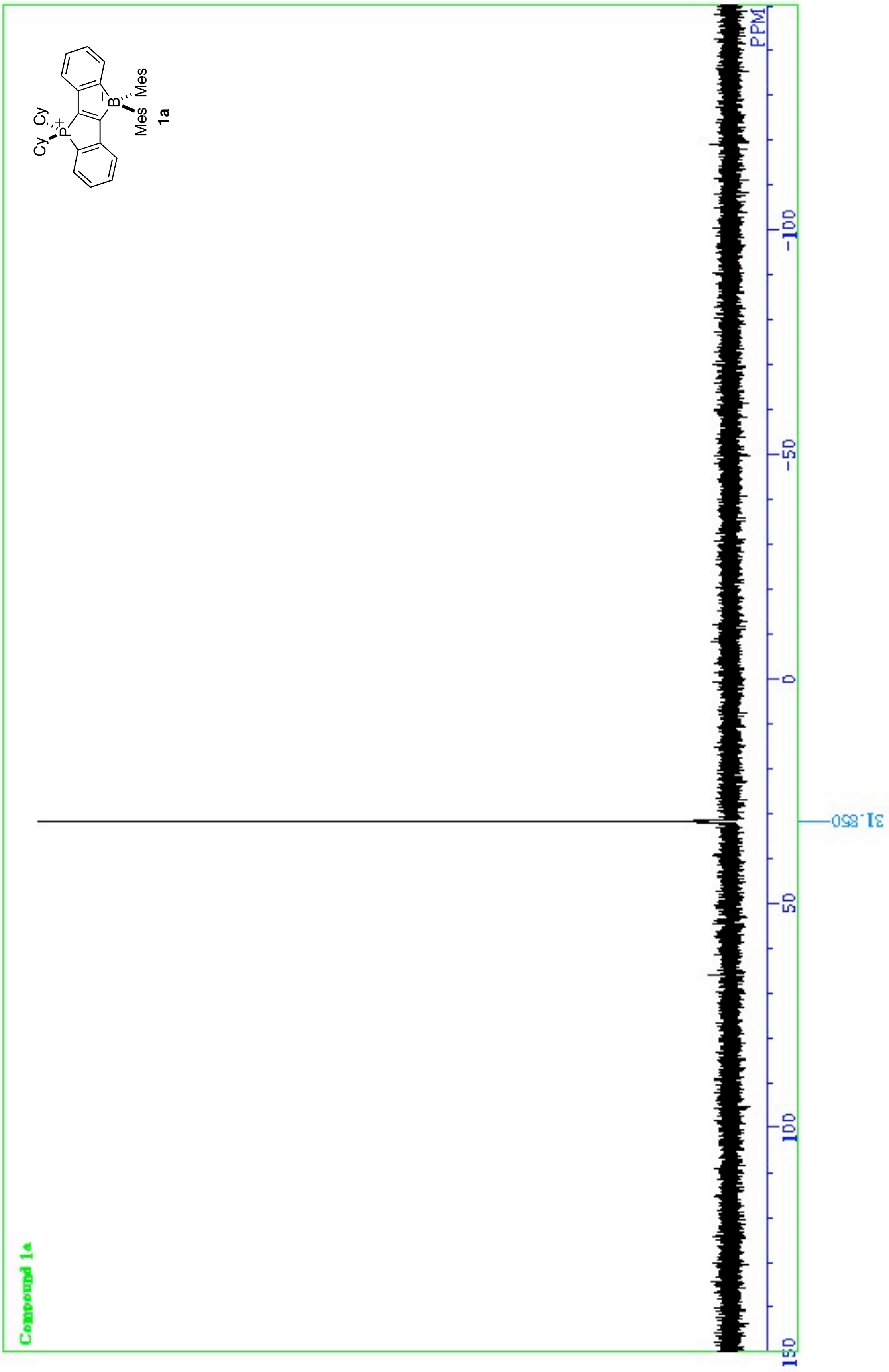


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **1a** (JEOL AL-400, 162 MHz, $CDCl_3$).

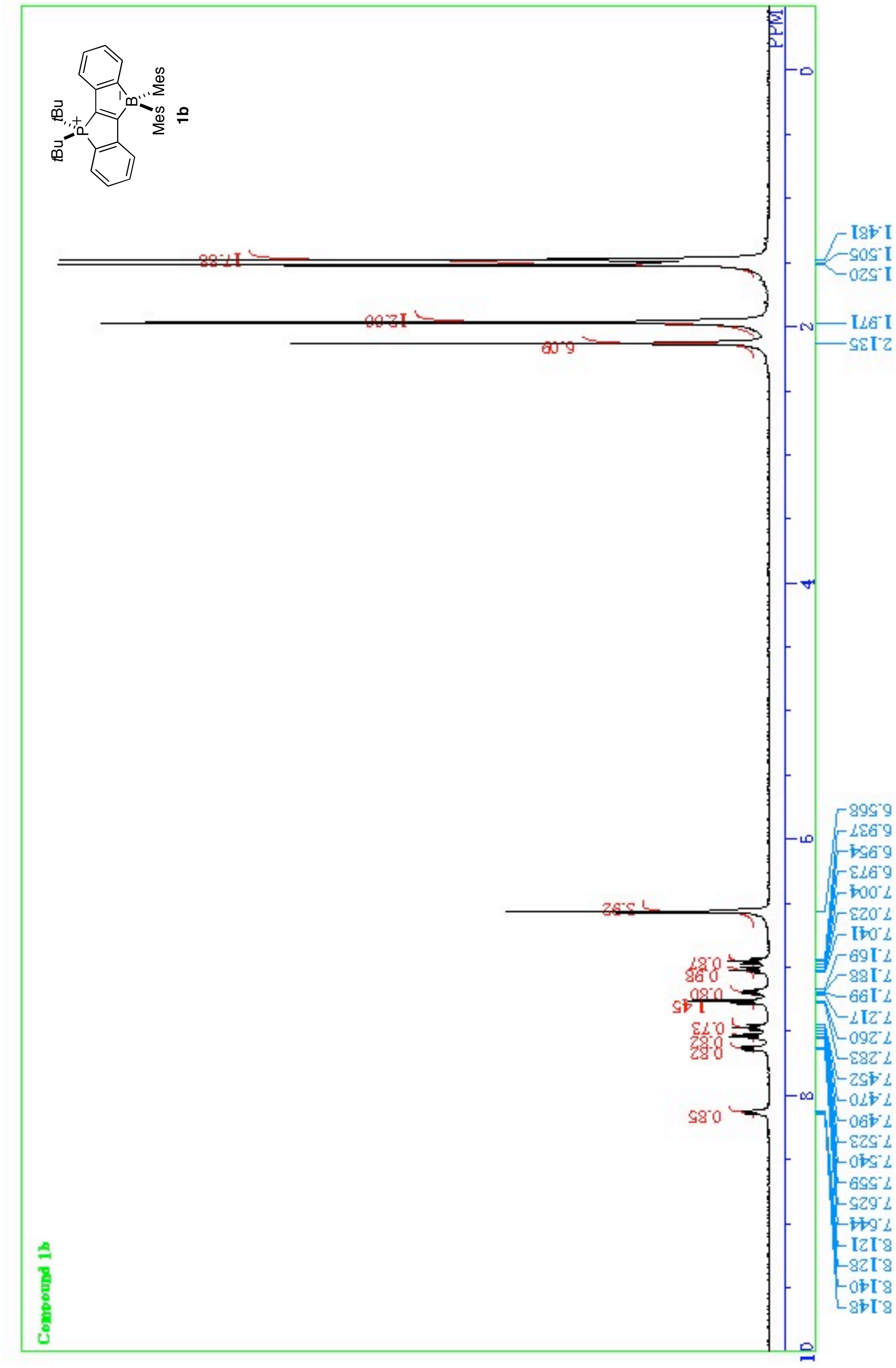


Figure S8. ^{1}H NMR spectrum of **1b** (JEOL AL-400, 400 MHz, CDCl$_3$).

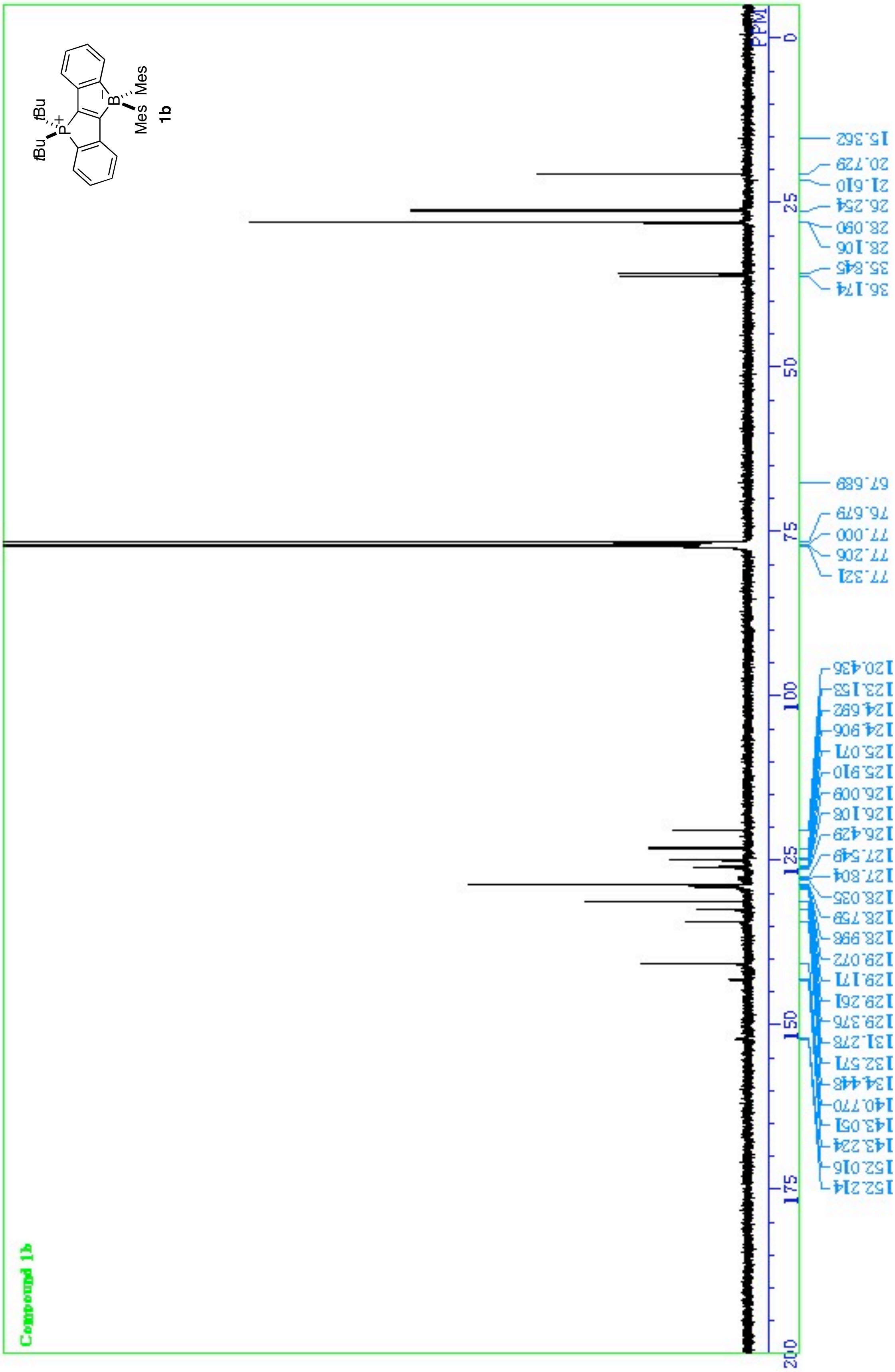


Figure S9. $^{13}C\{^1H\}$ NMR spectrum of **1b** (JEOL AL-400, 100 MHz, $CDCl_3$).

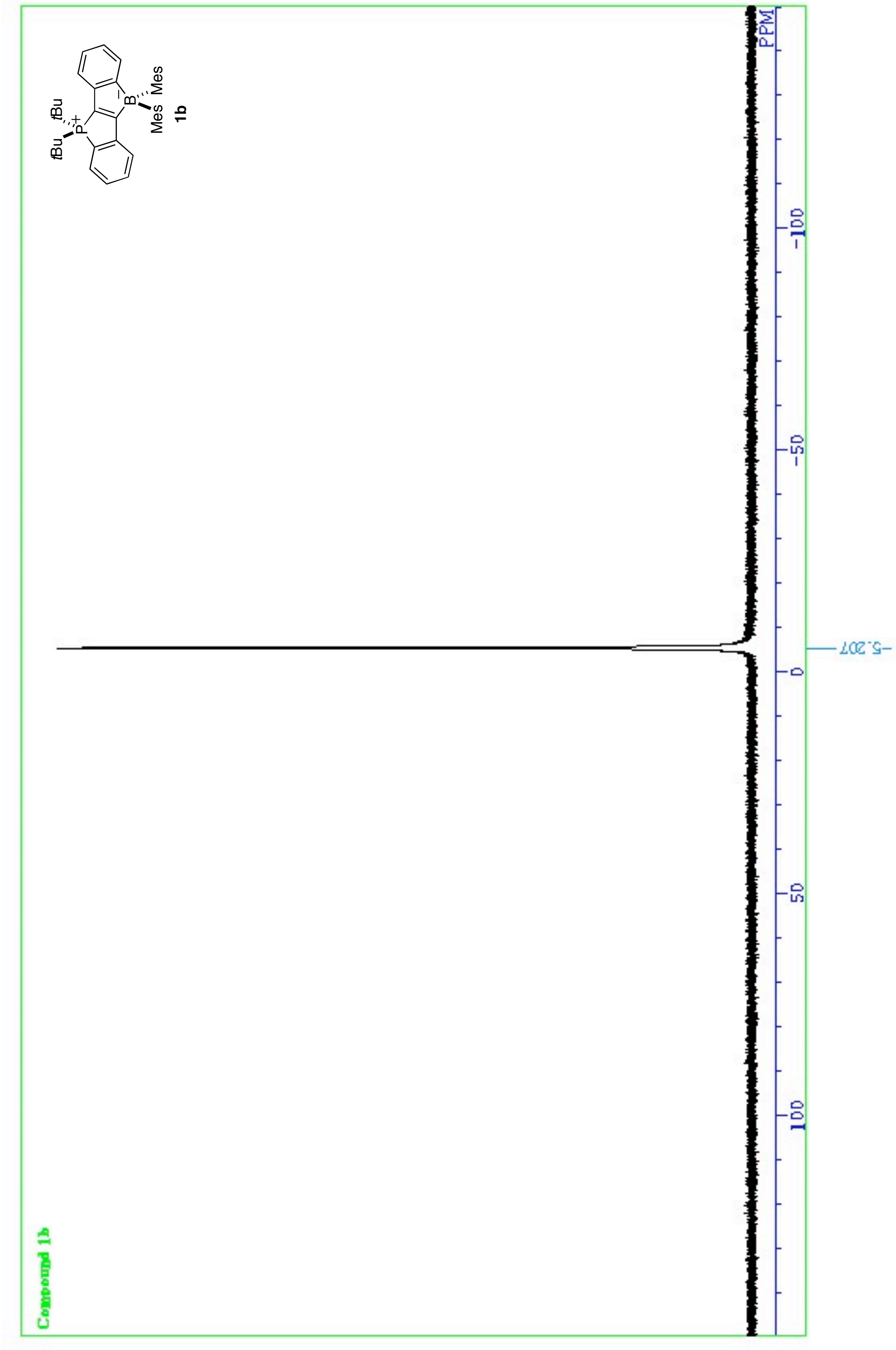


Figure S10. $^{11}B\{^1H\}$ NMR spectrum of **1b** (JEOL AL-400, 128 MHz, $CDCl_3$).

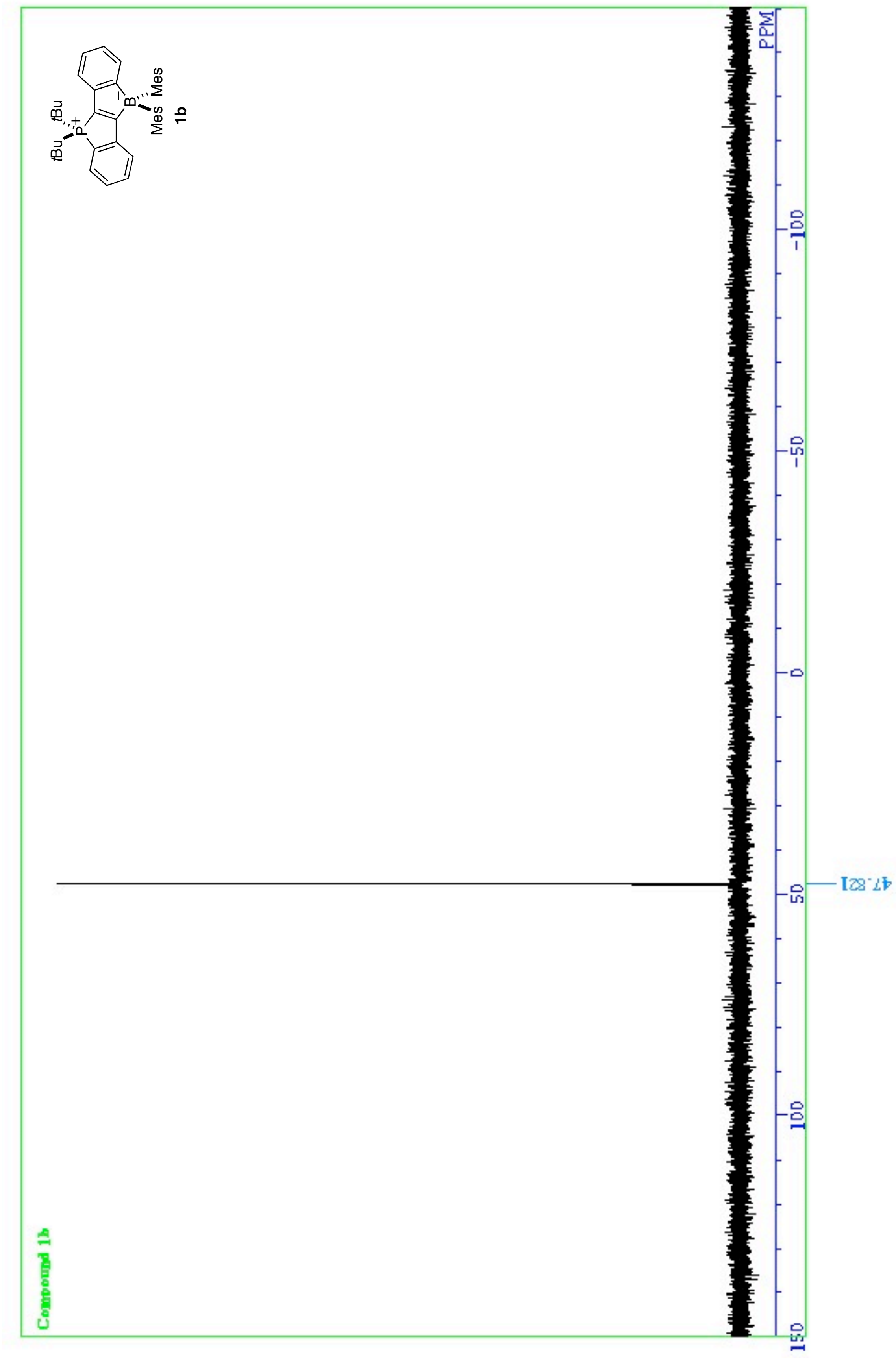


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** (JEOL AL-400, 162 MHz, $CDCl_3$).

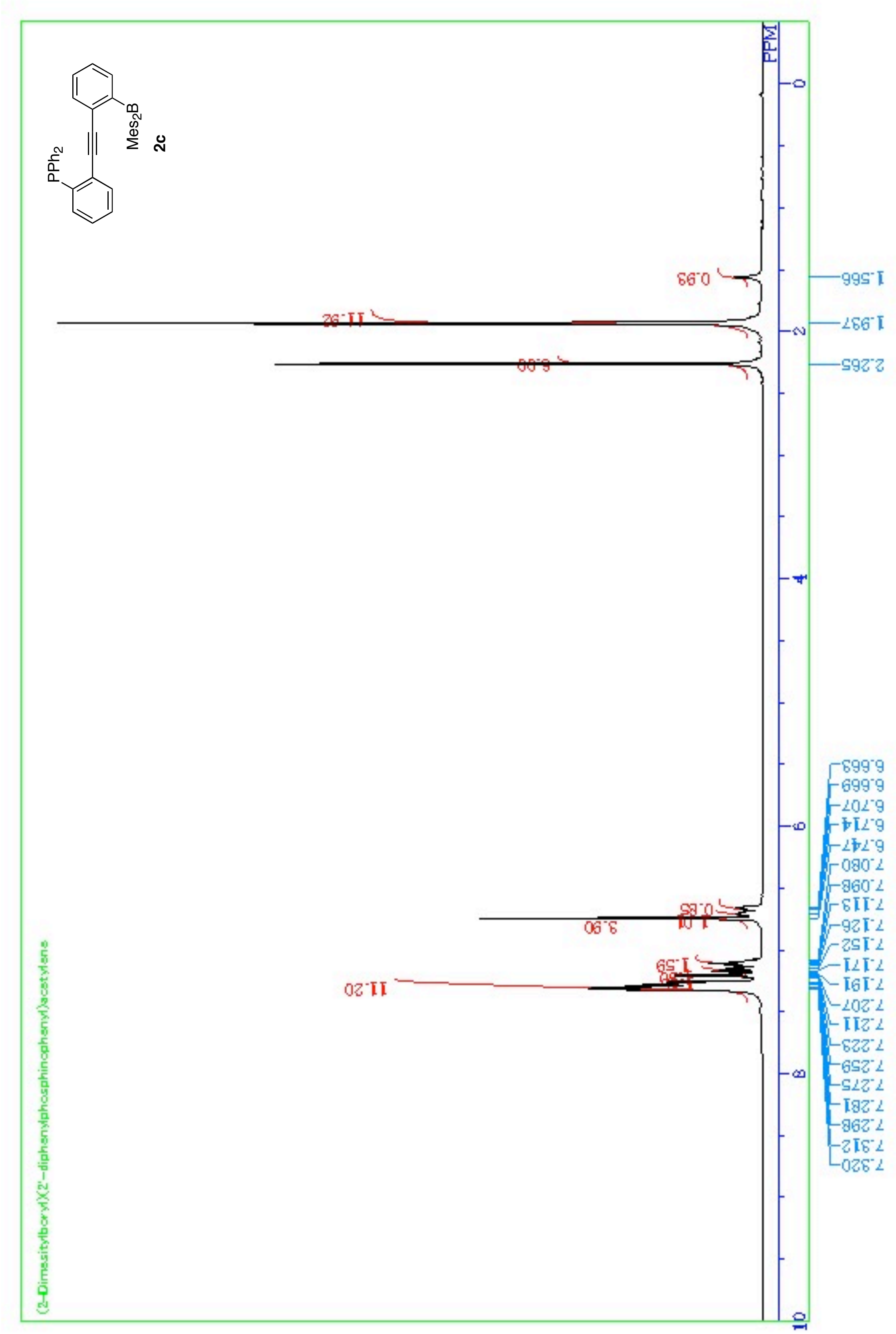


Figure S12. ^{1}H NMR spectrum of **2c** (JEOL AL-400, 400 MHz, $CDCl_3$).

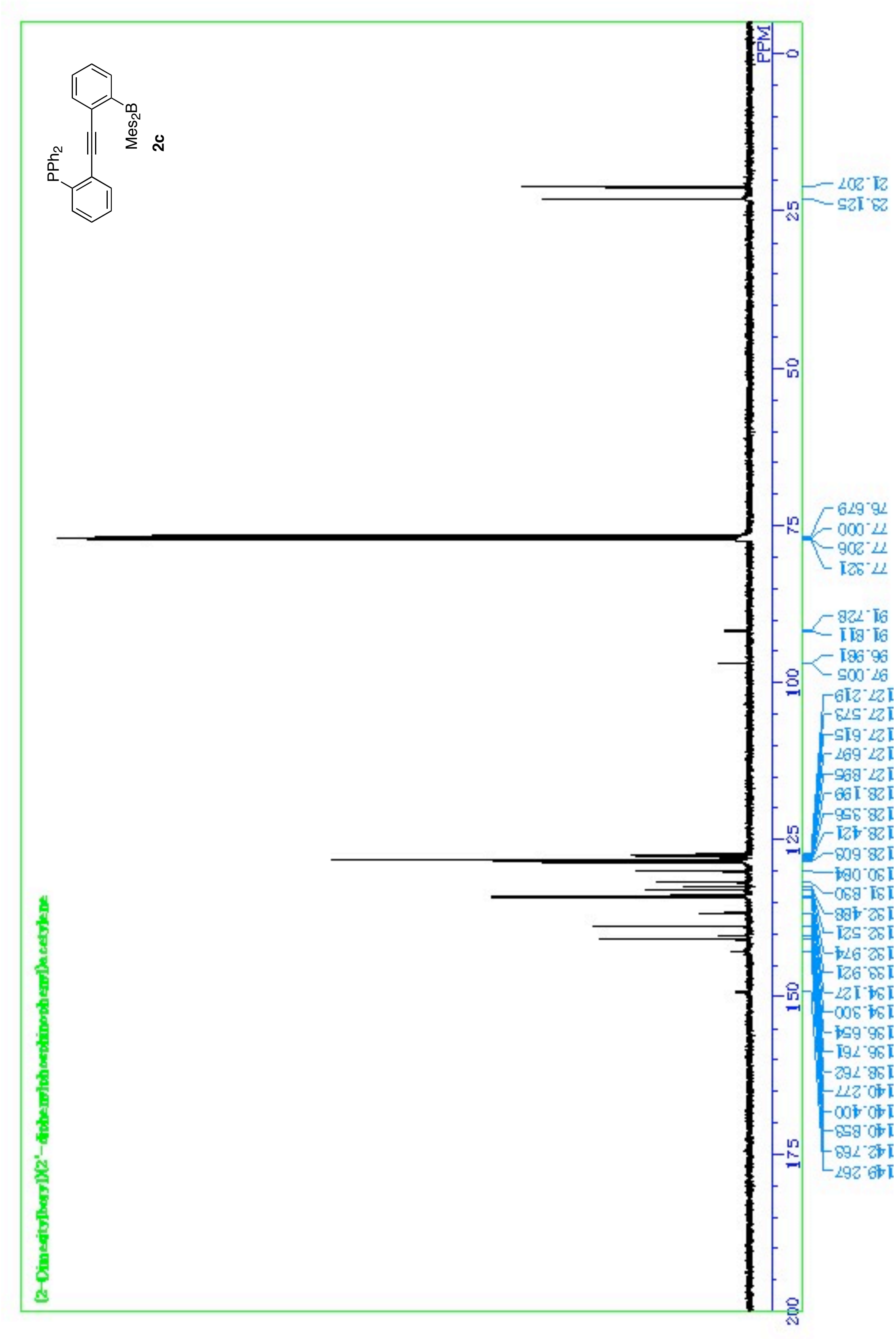


Figure S13. $^{13}C\{^1H\}$ NMR spectrum of **2c** (JEOL AL-400, 100 MHz, $CDCl_3$).

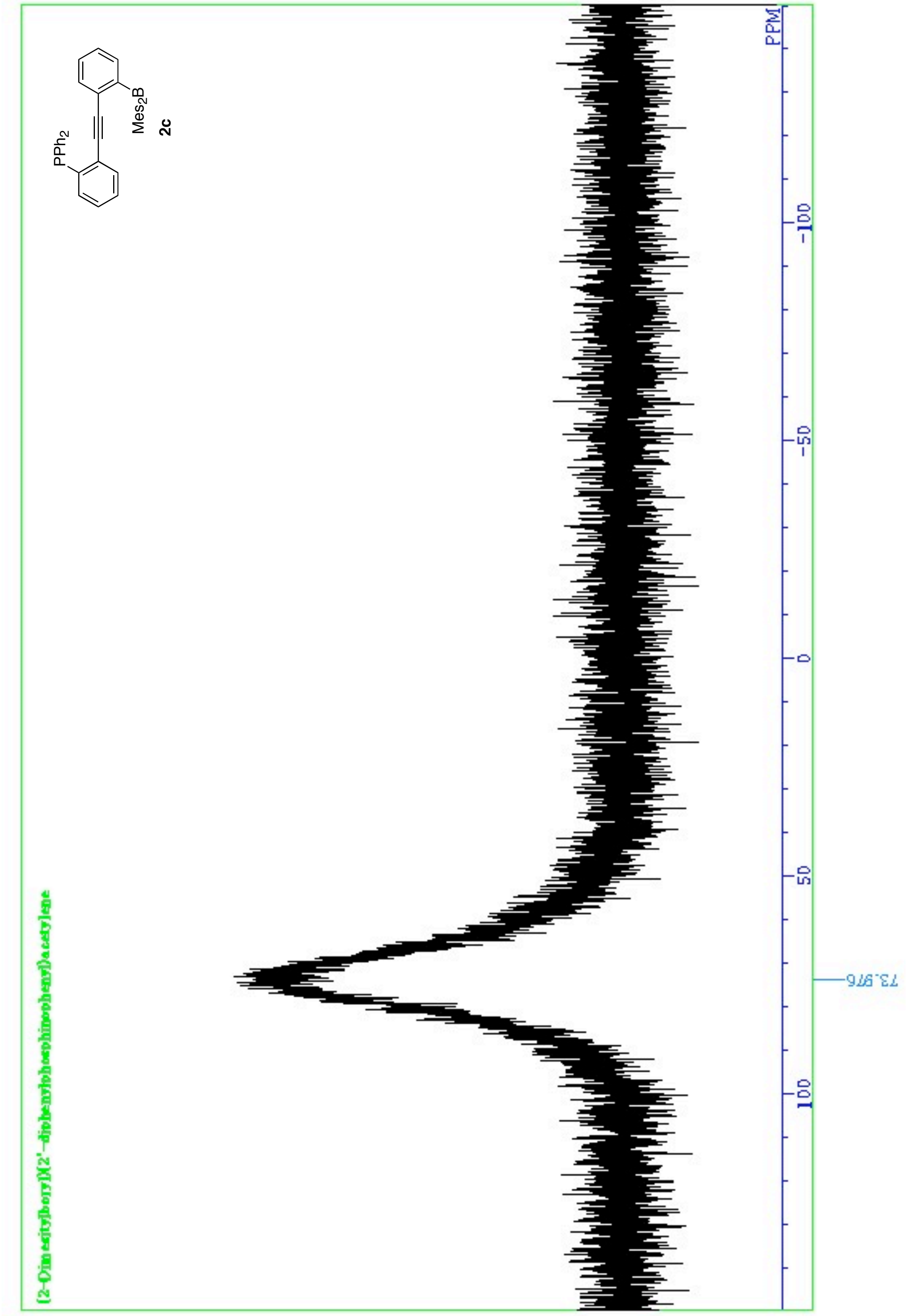


Figure S14. ${}^{11}B\{{}^{1}H\}$ NMR spectrum of **2c** (JEOL AL-400, 128 MHz, $CDCl_3$).

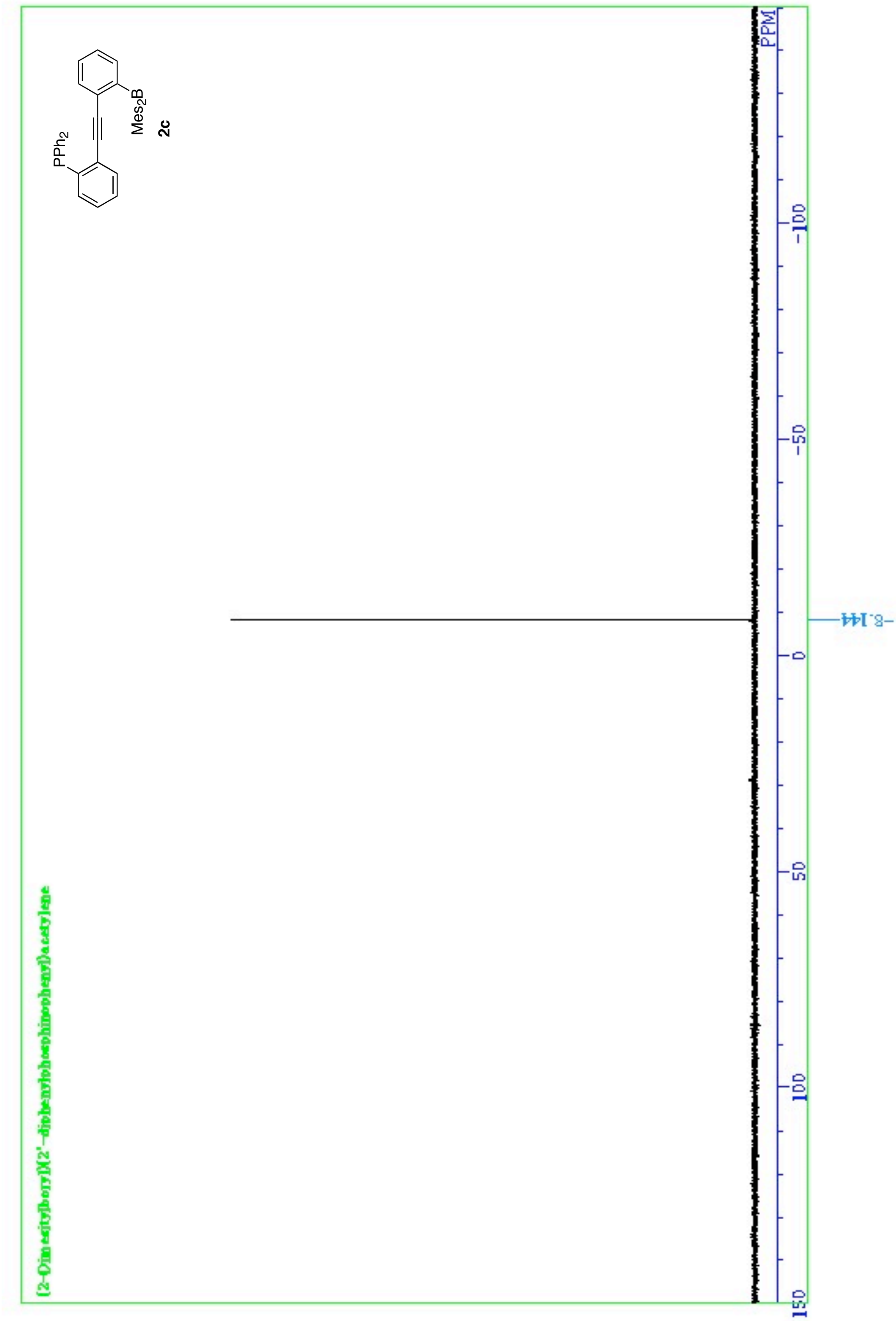


Figure S15. $^{31}P\{^1H\}$ NMR spectrum of **2c** (JEOL AL-400, 162 MHz, $CDCl_3$).

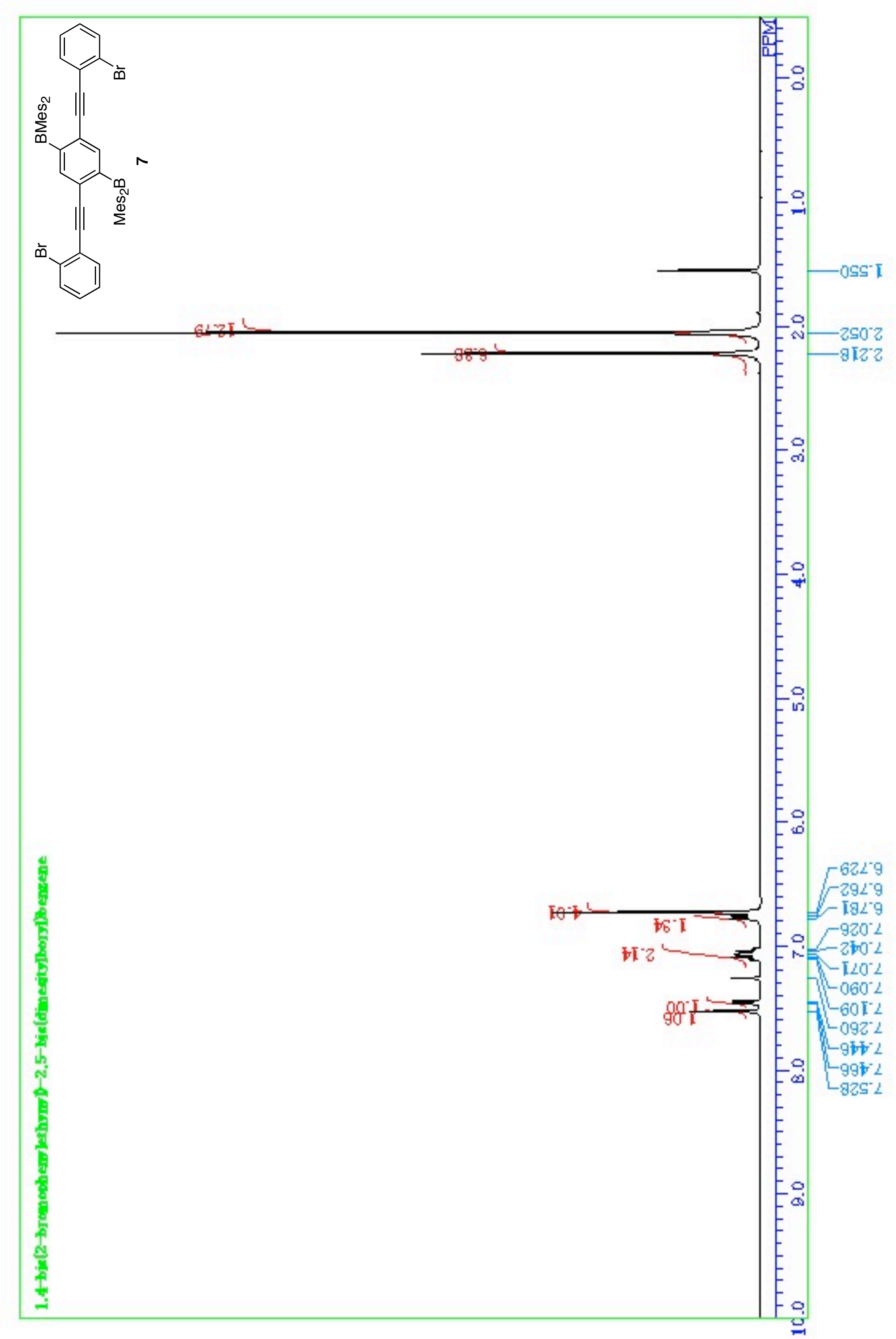


Figure S16. ^{1}H NMR spectrum of **7** (JEOL AL-400, 400 MHz, $CDCl_3$).

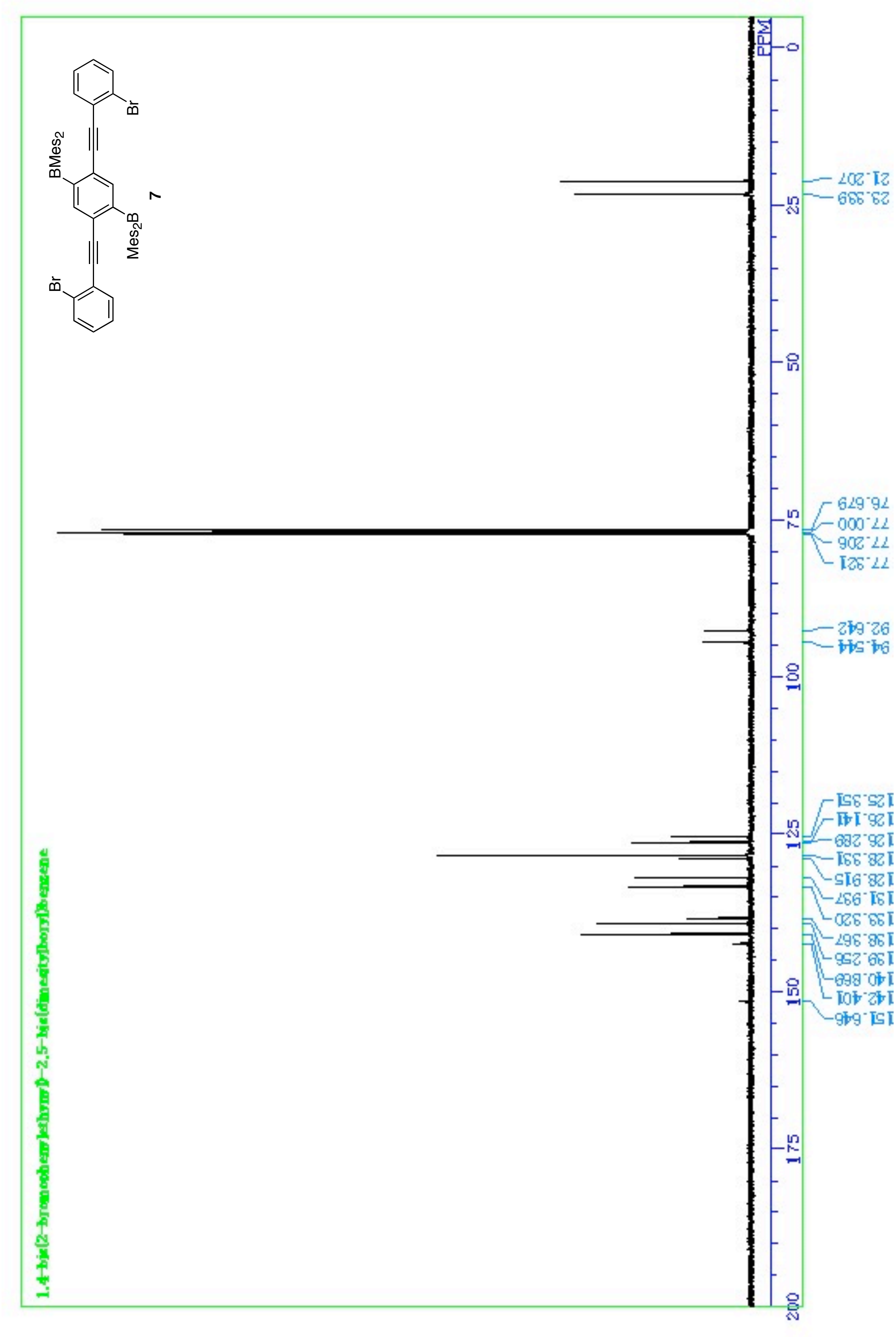


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **7** (JEOL AL-400, 100 MHz, $CDCl_3$).

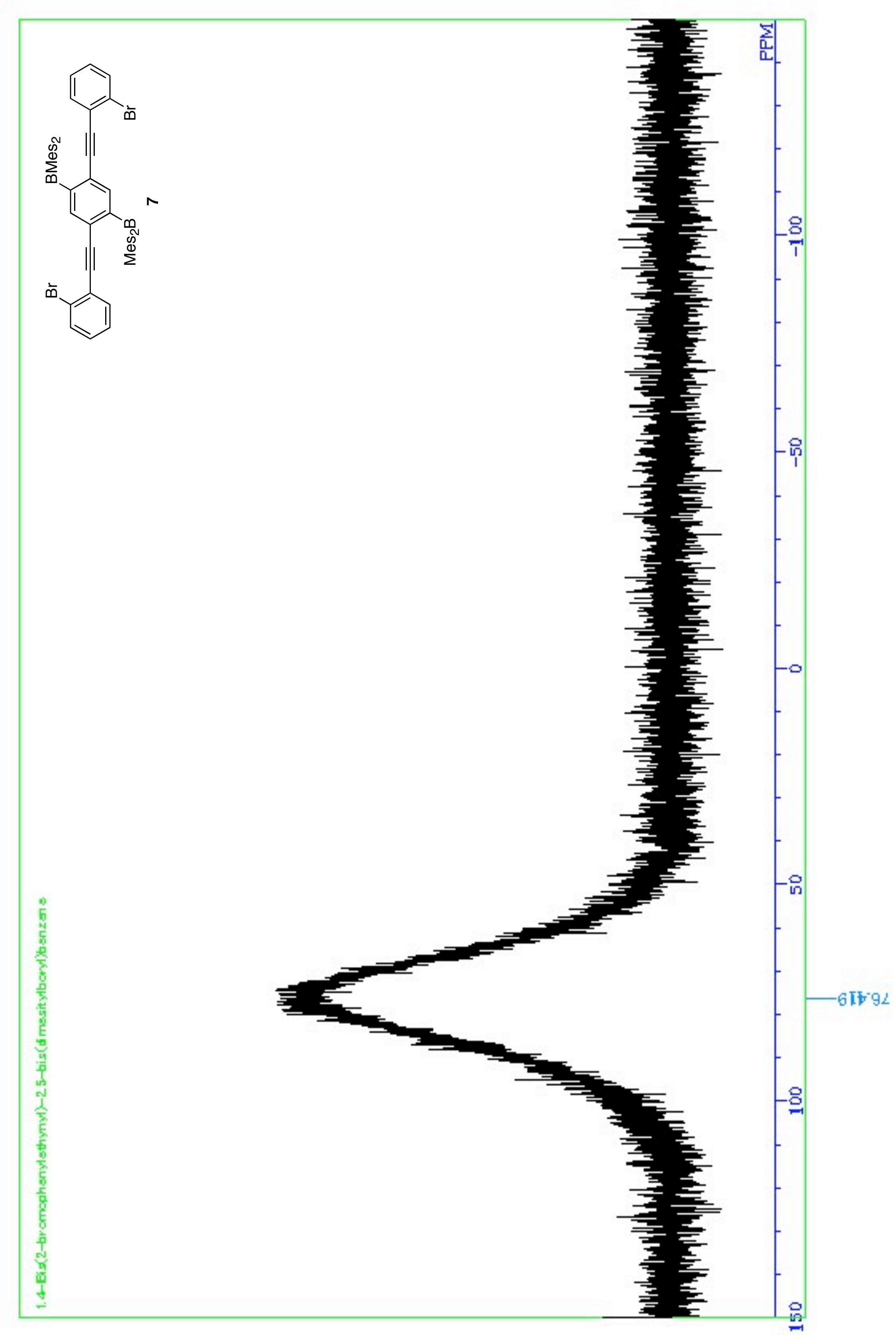


Figure S18. $^{11}B\{^{1}H\}$ NMR spectrum of **7** (JEOL A-400, 128 MHz, $CDCl_3$).

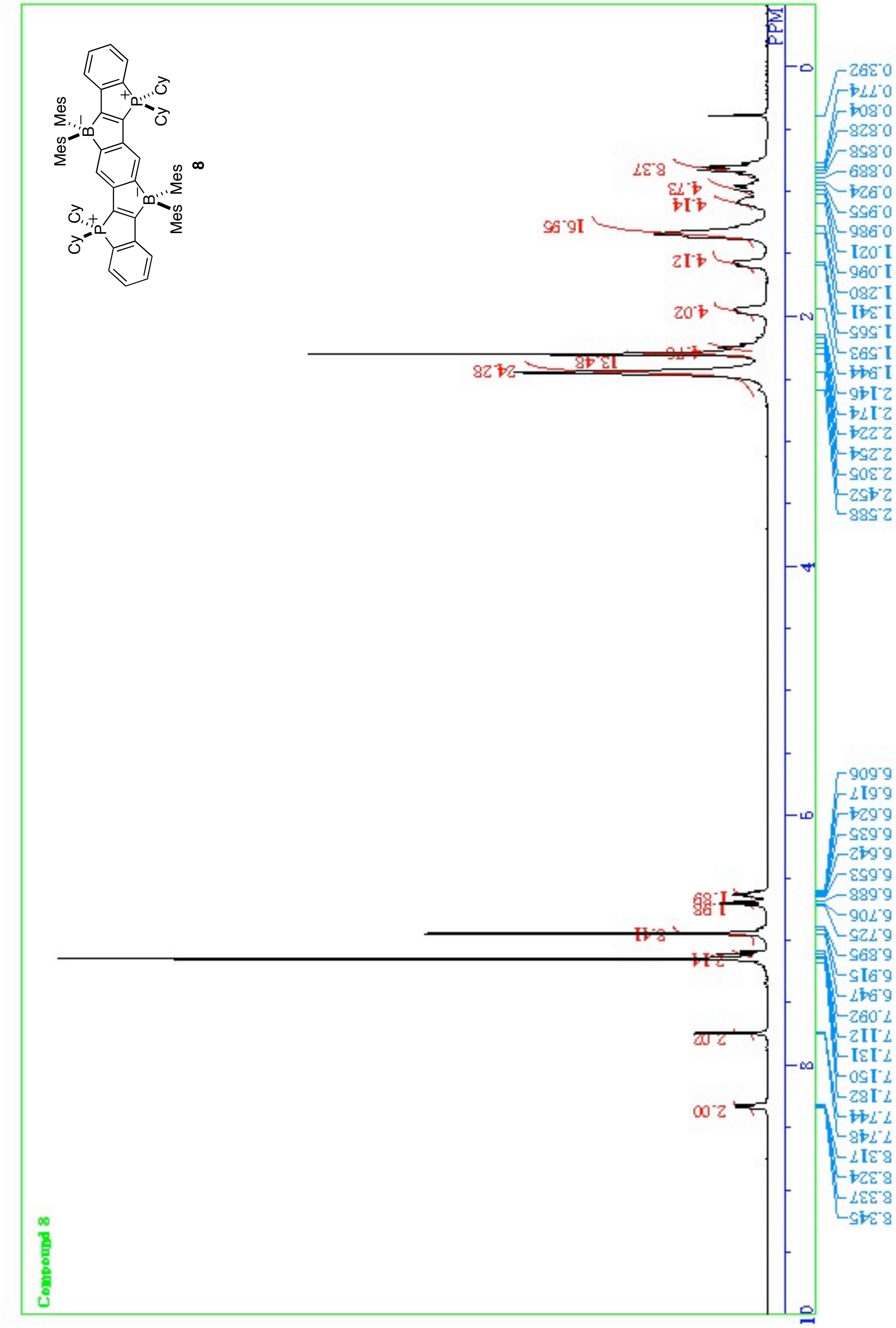


Figure S19. ^{1}H NMR spectrum of **8** (JEOL AL-400, 400 MHz, C_6D_6).

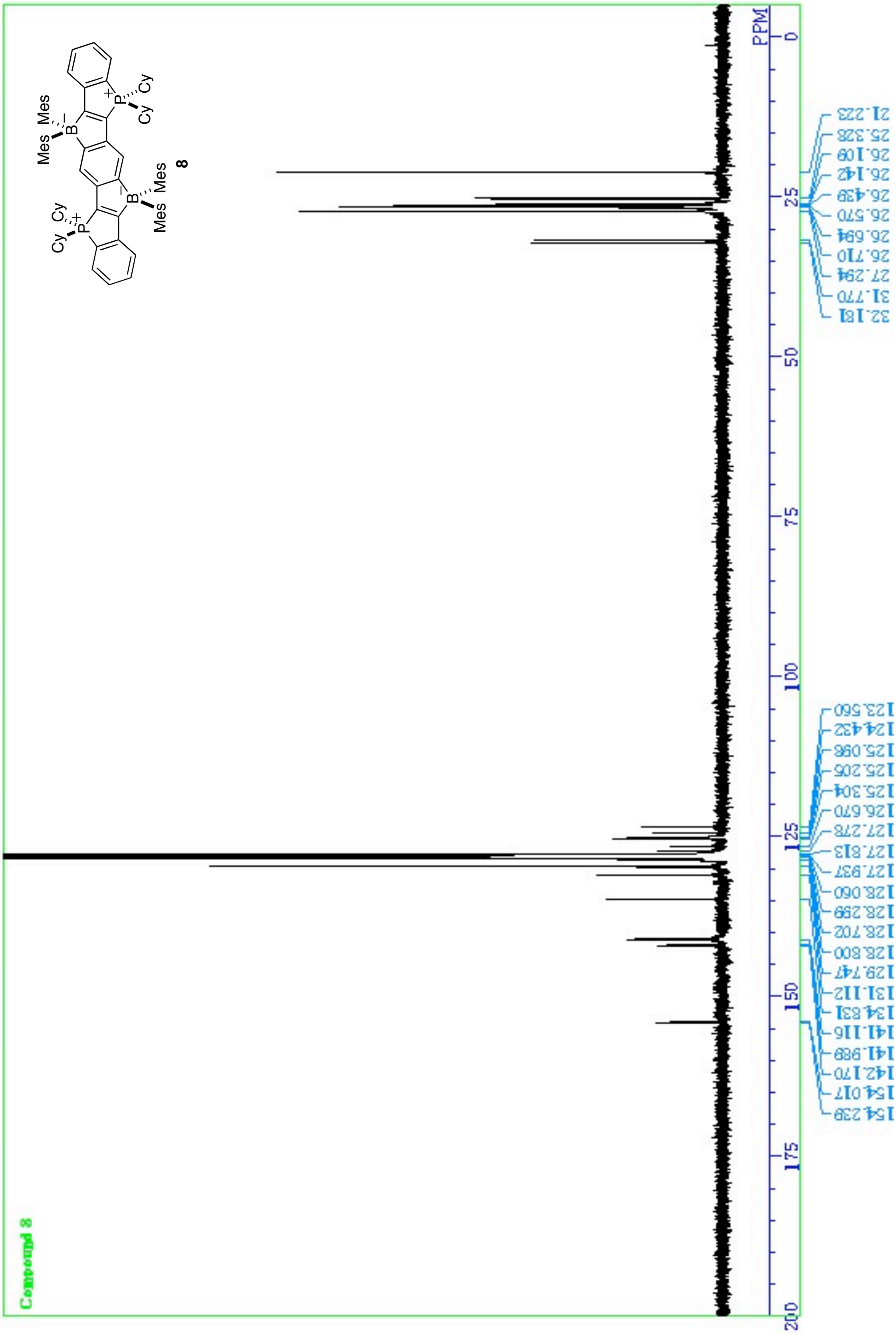


Figure S20. $^{13}C\{^1H\}$ NMR spectrum of **8** (JEOL A-400, 100 MHz, C_6D_6).

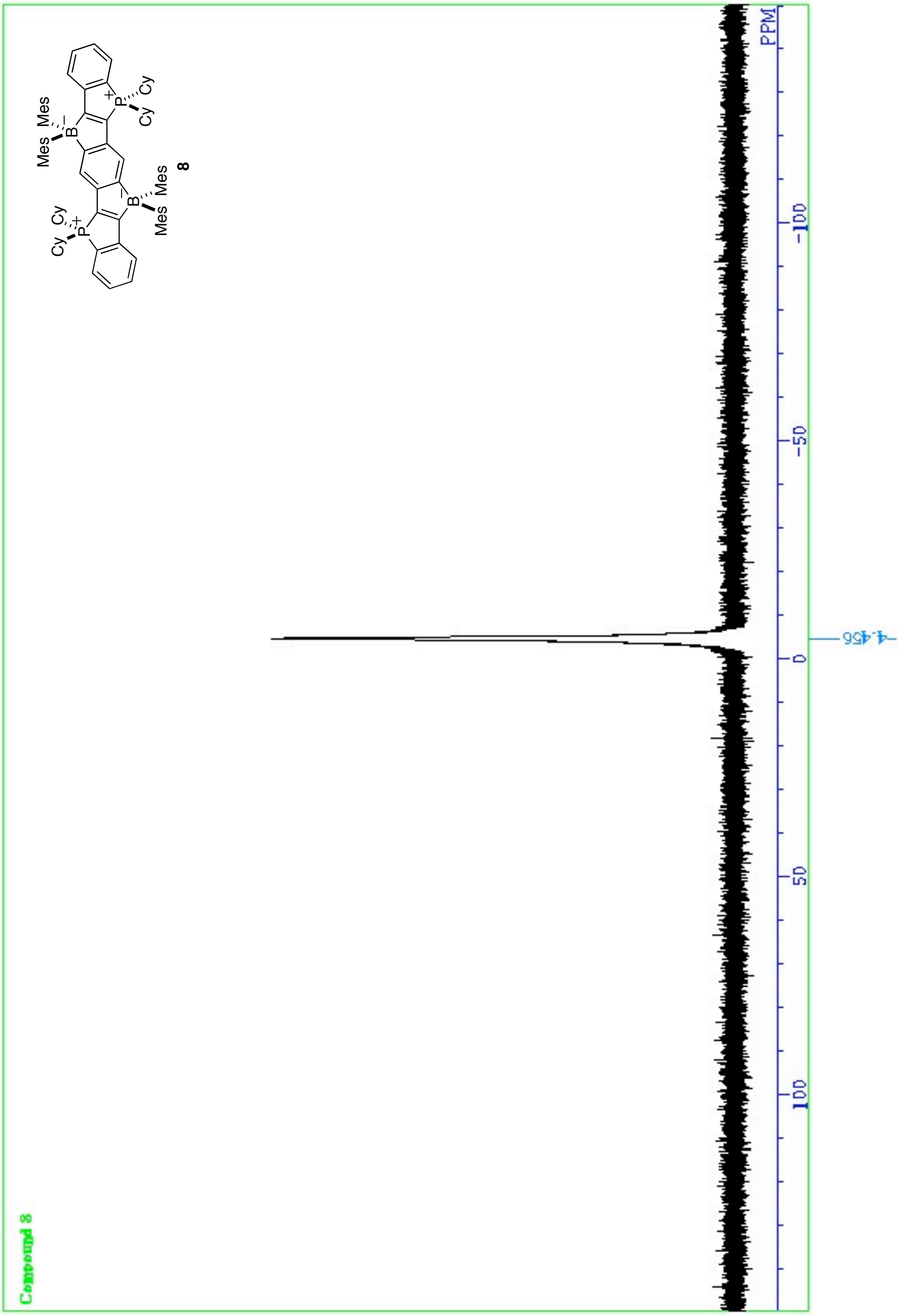


Figure S21. $^{11}B\{^{1}H\}$ NMR spectrum of **8** (JEOL AL-400, 128 MHz, C_6D_6).

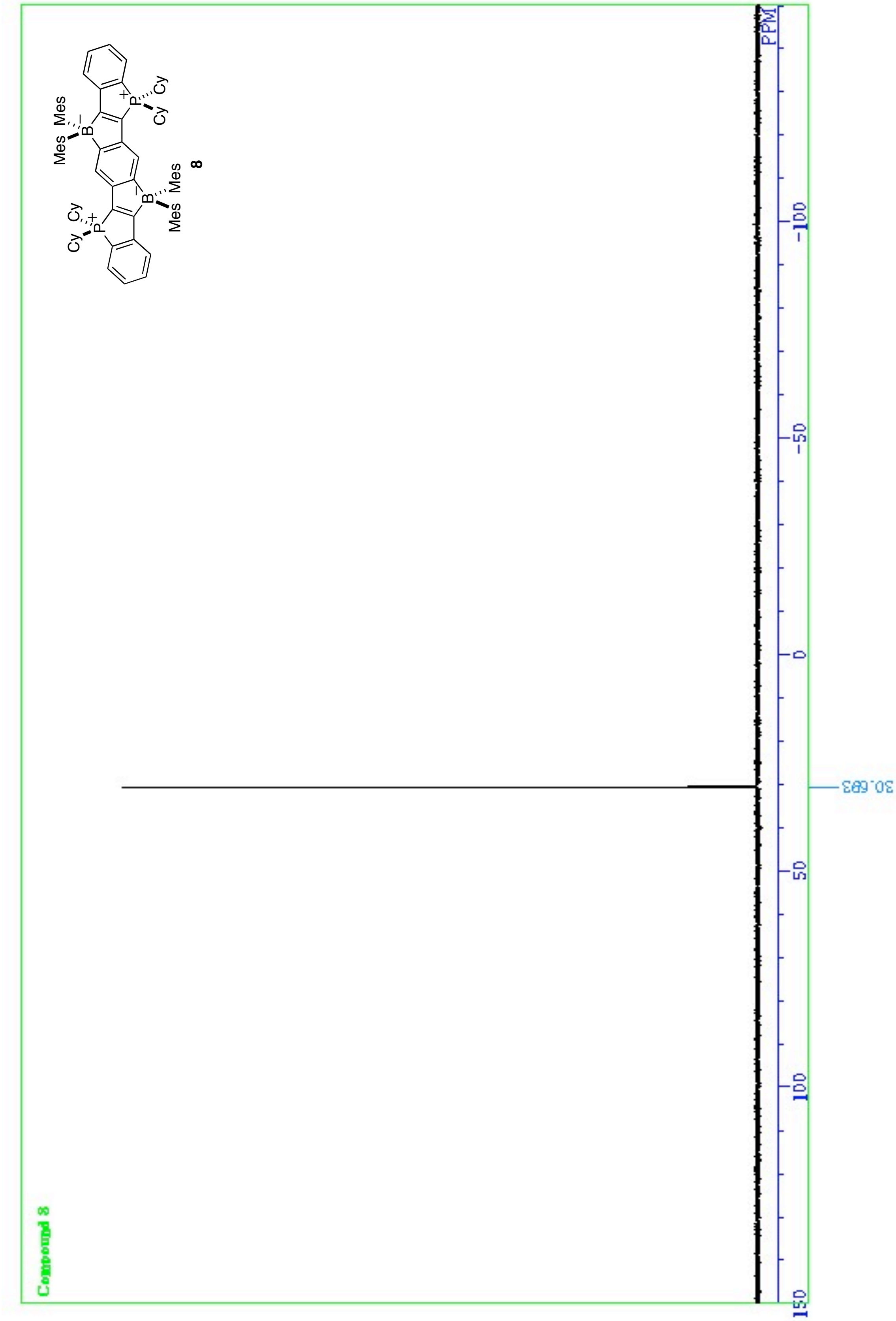


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **8** (JEOL AL-400, 162 MHz, C_6D_6).

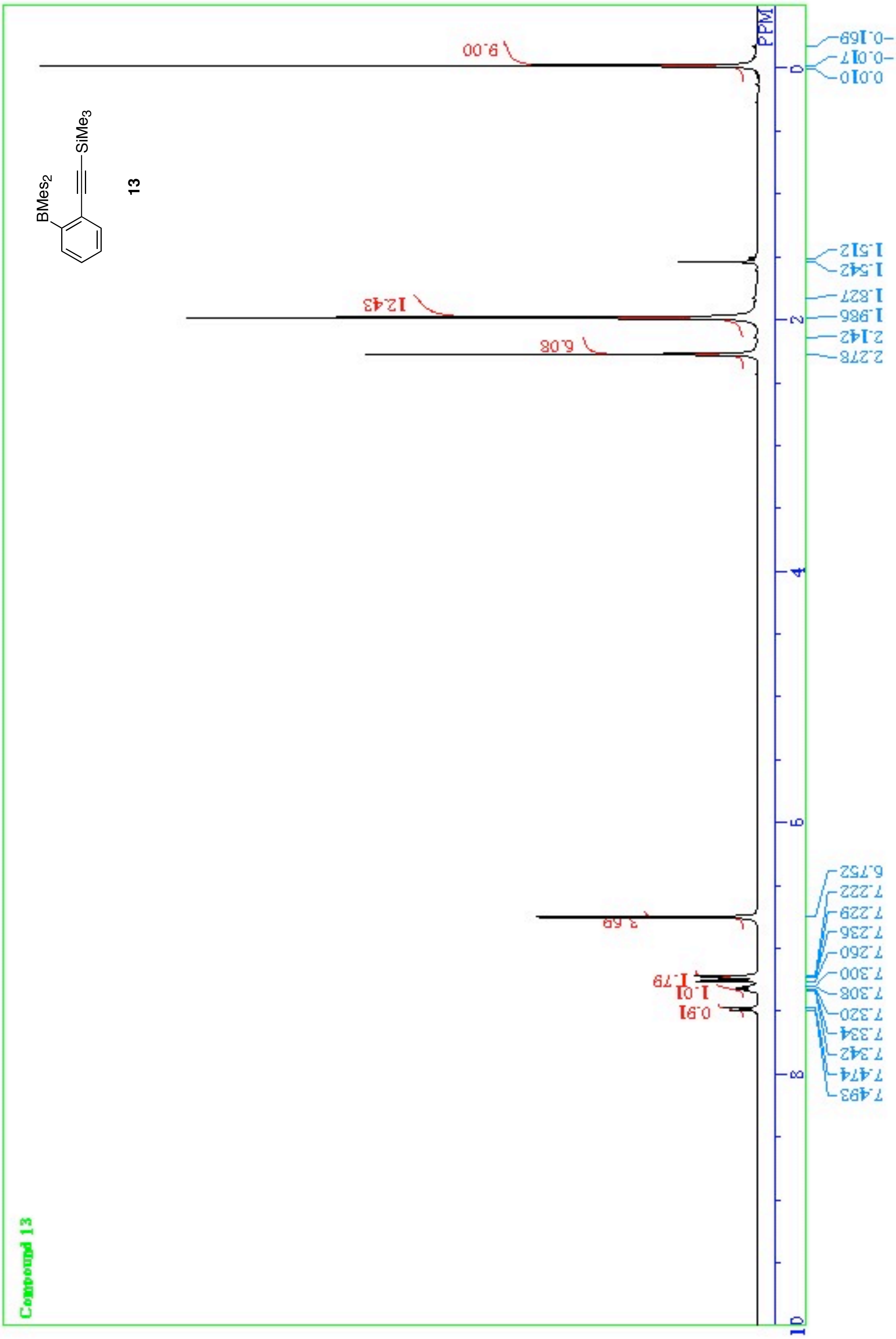


Figure S23. ^{1}H NMR spectrum of **13** (JEOL AL-400, 400 MHz, CDCl$_3$).

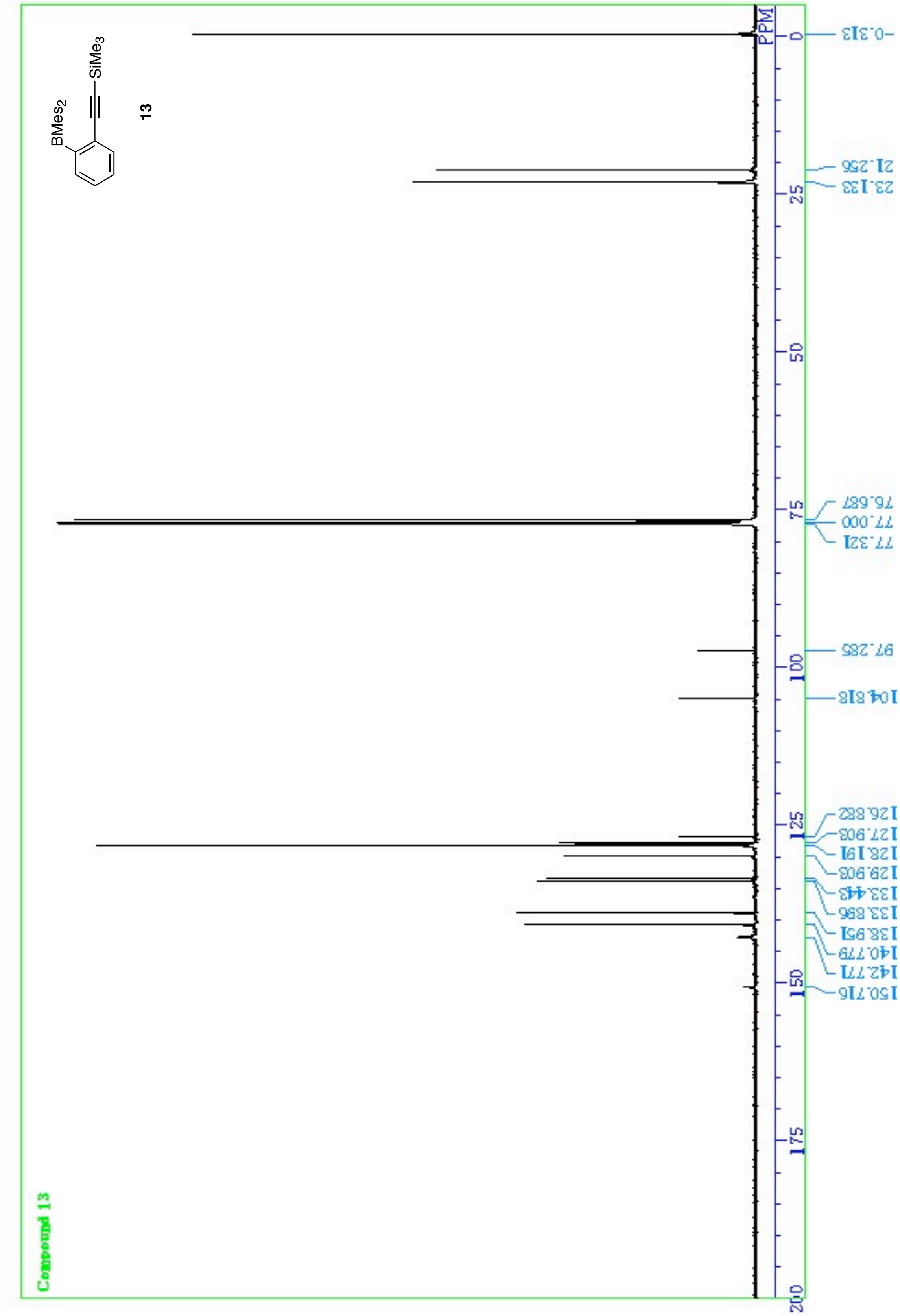


Figure S24. $^{13}C\{^1H\}$ NMR spectrum of **13** (JEOL AL-400, 100 MHz, $CDCl_3$).

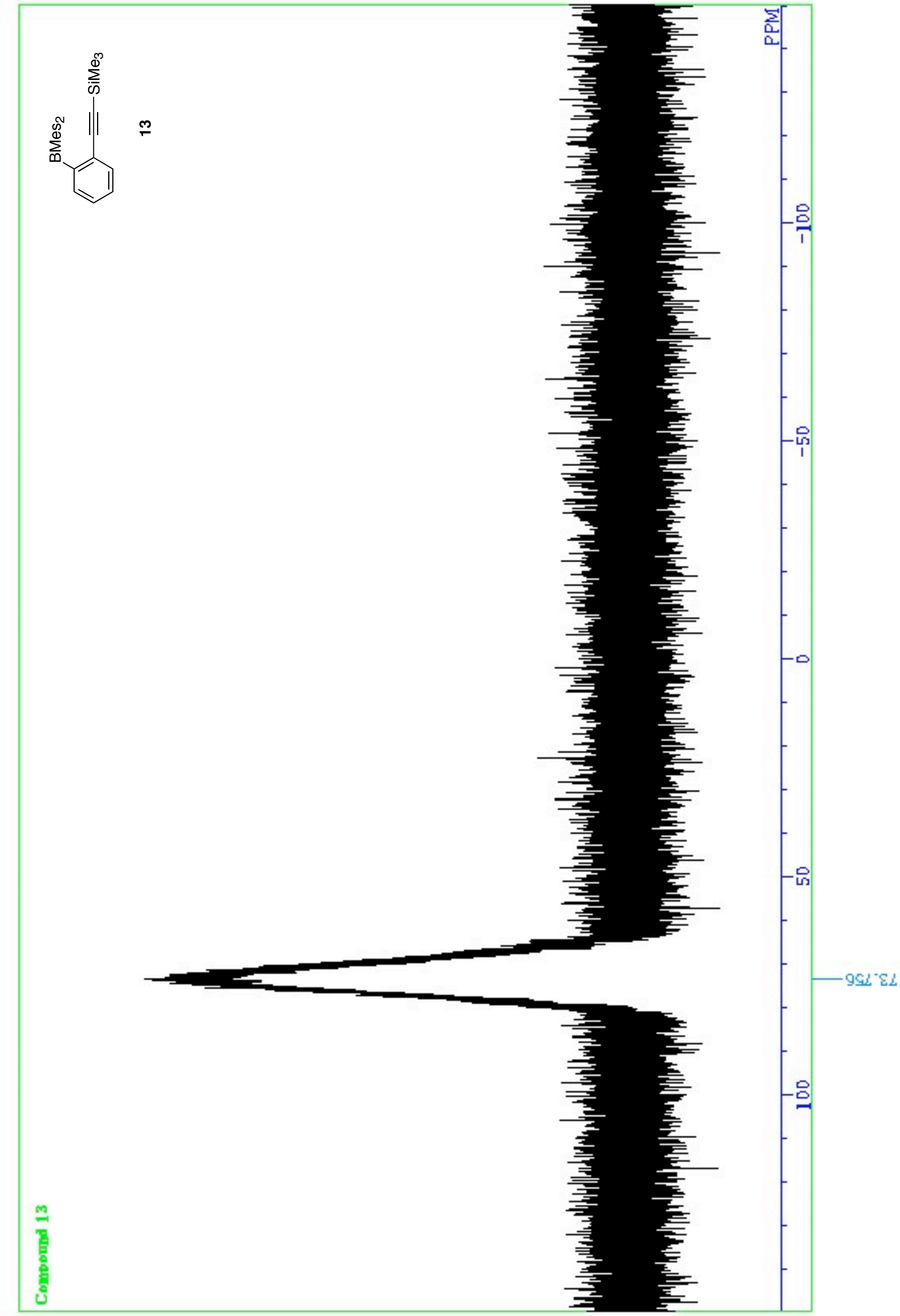


Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum of **13** (JEOL AL-400, 128 MHz, $CDCl_3$).

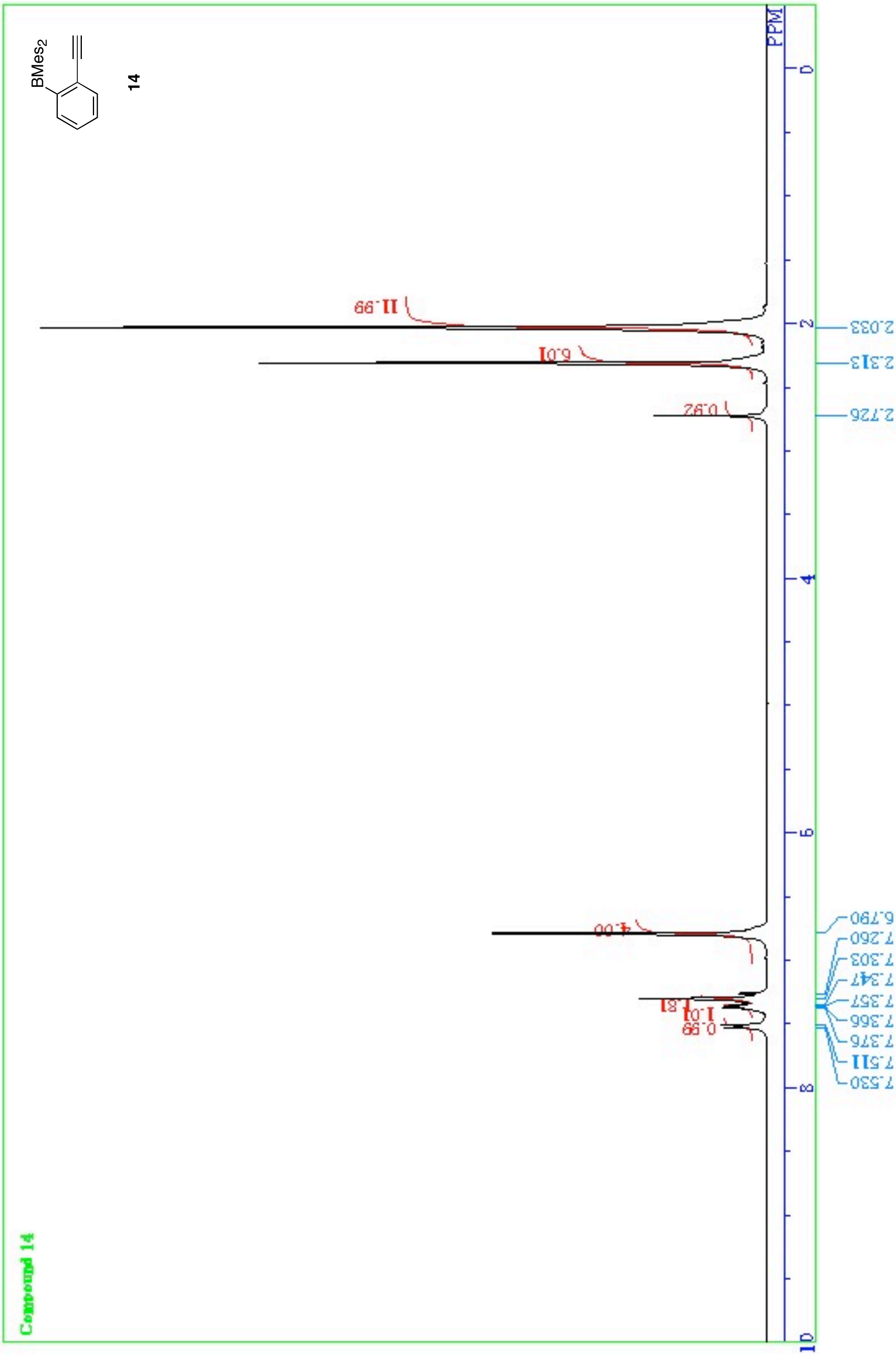


Figure S26. ^{1}H NMR spectrum of **14** (JEOL AL-400, 400 MHz, $CDCl_3$).

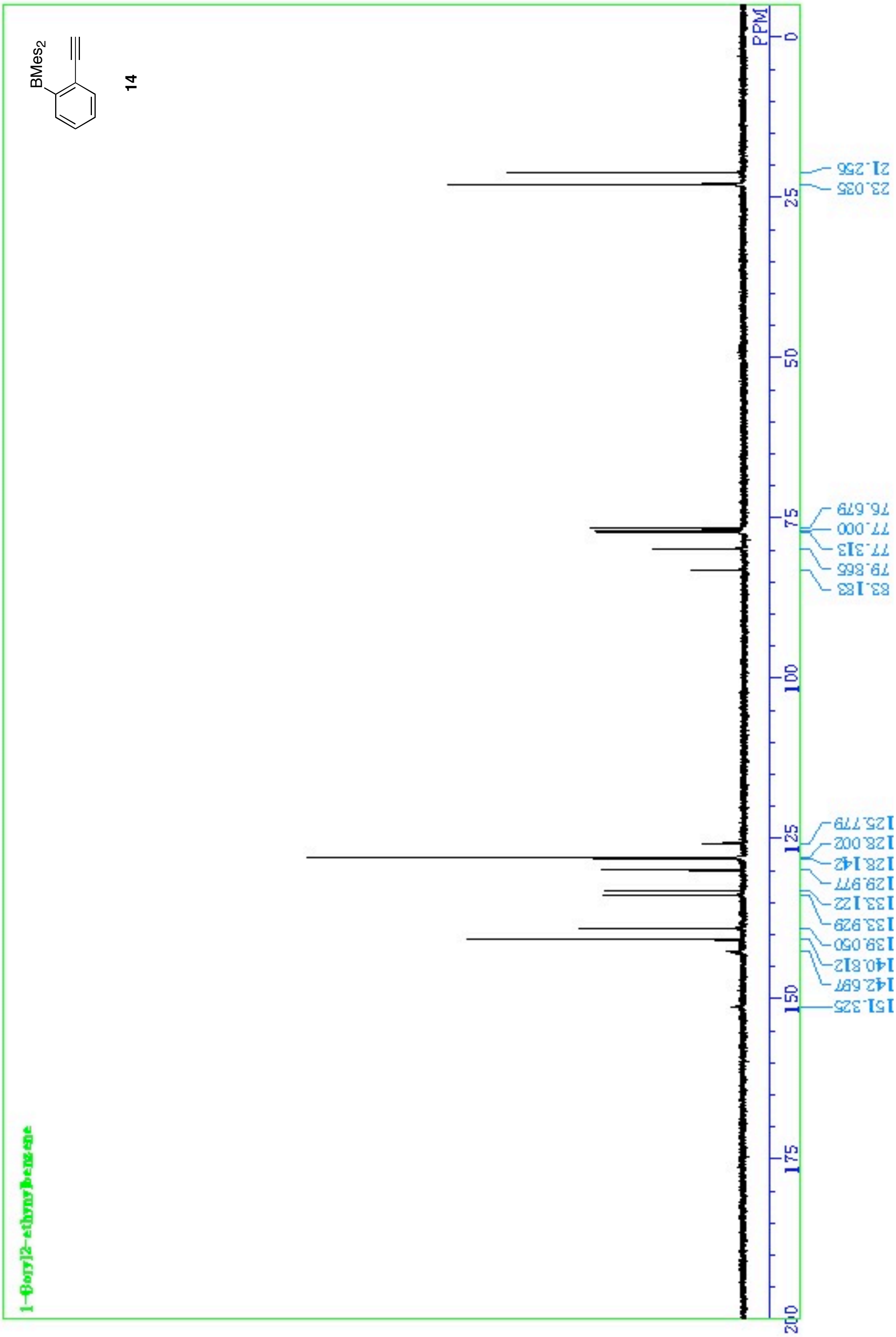


Figure S27. $^{13}C\{^1H\}$ NMR spectrum of **14** (JEOL AL-400, 100 MHz, $CDCl_3$).

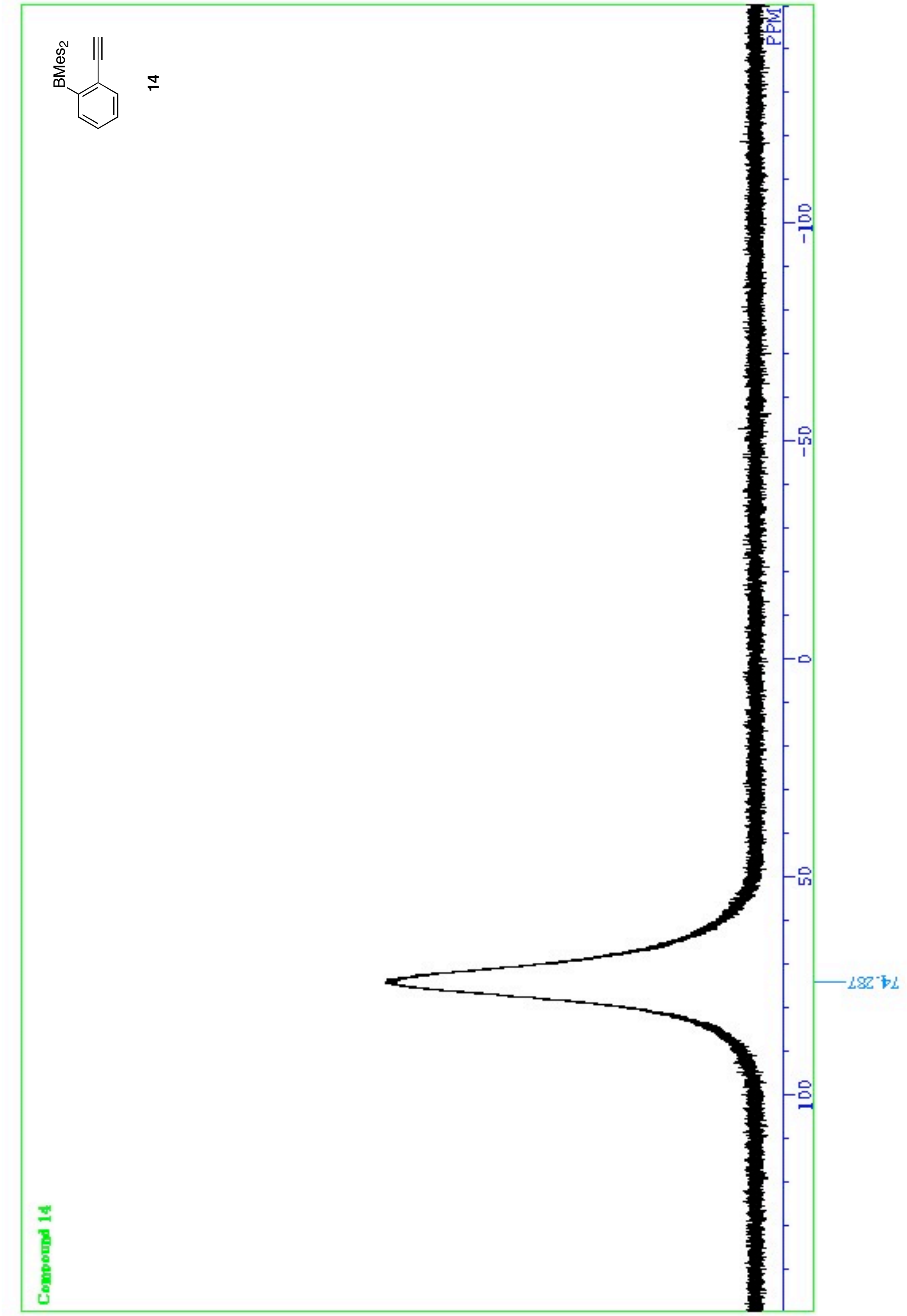


Figure S28. $^{11}B\{^{1}H\}$ NMR spectrum of **14** (JEOL AL-400, 128 MHz, $CDCl_3$).

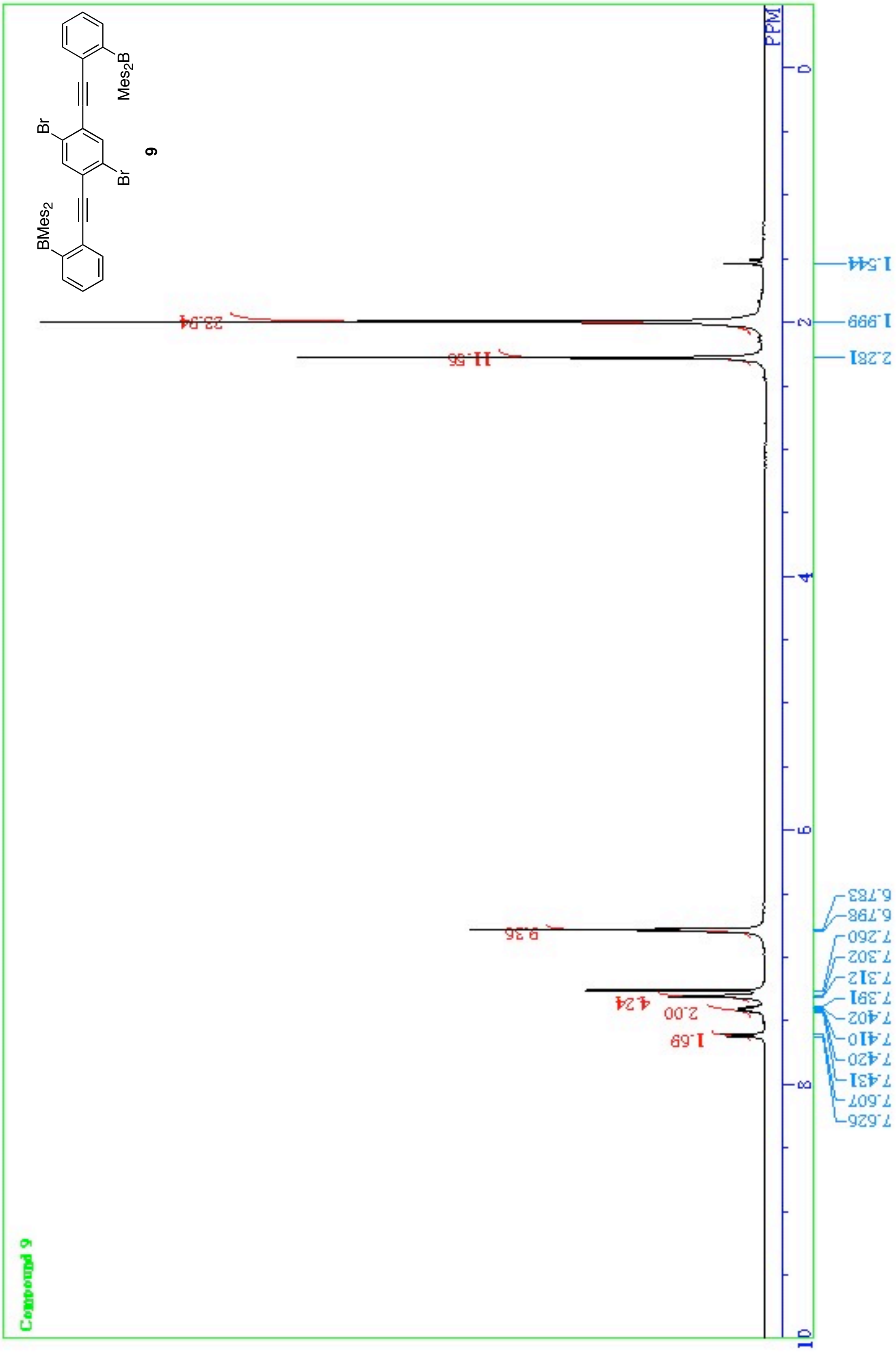


Figure S29. ^{1}H NMR spectrum of **9** (JEOL AL-400, 400 MHz, CDCl$_3$).

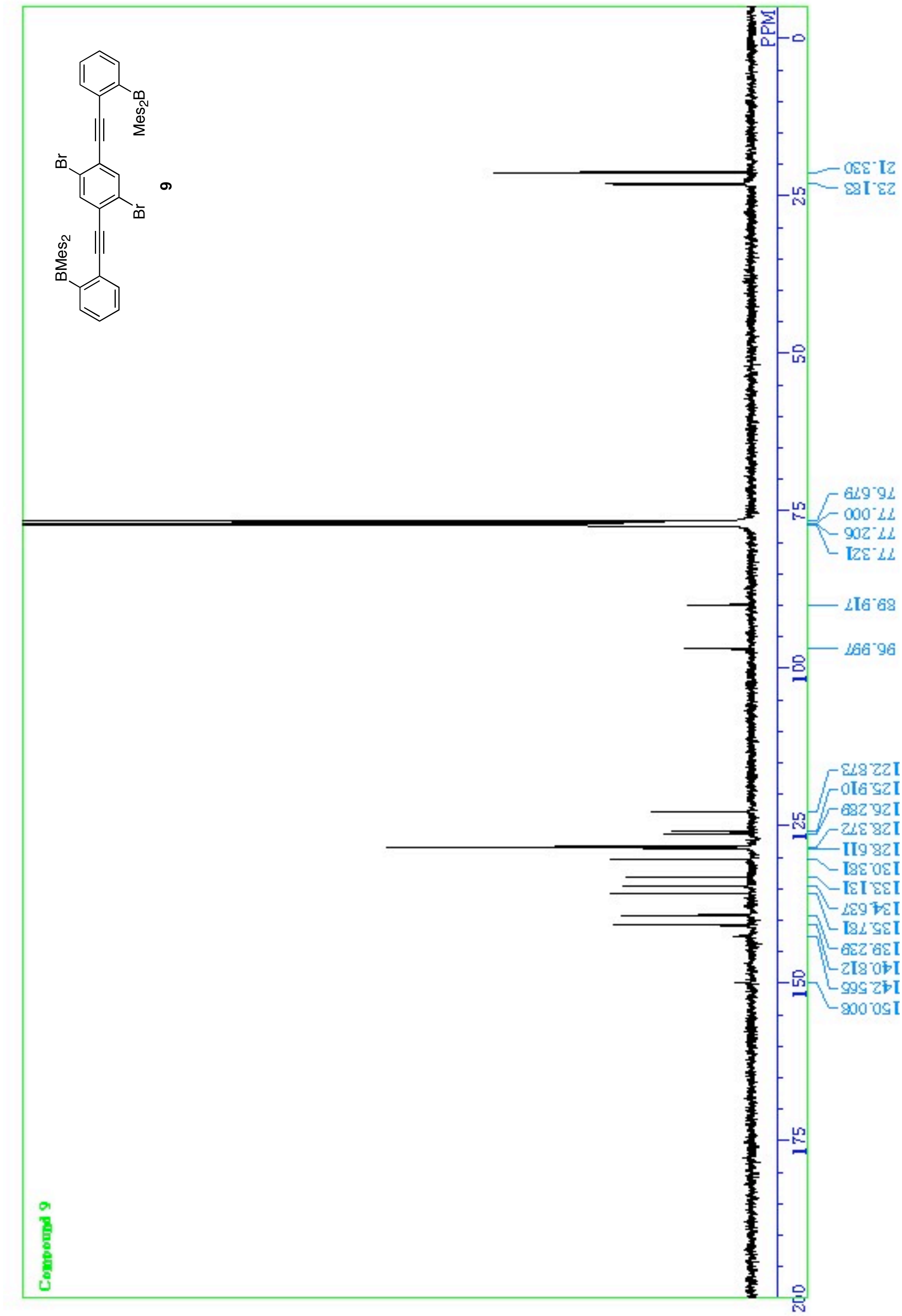


Figure S30. $^{13}C\{^1H\}$ NMR spectrum of **9** (JEOL AL-400, 100 MHz, CDCl$_3$).

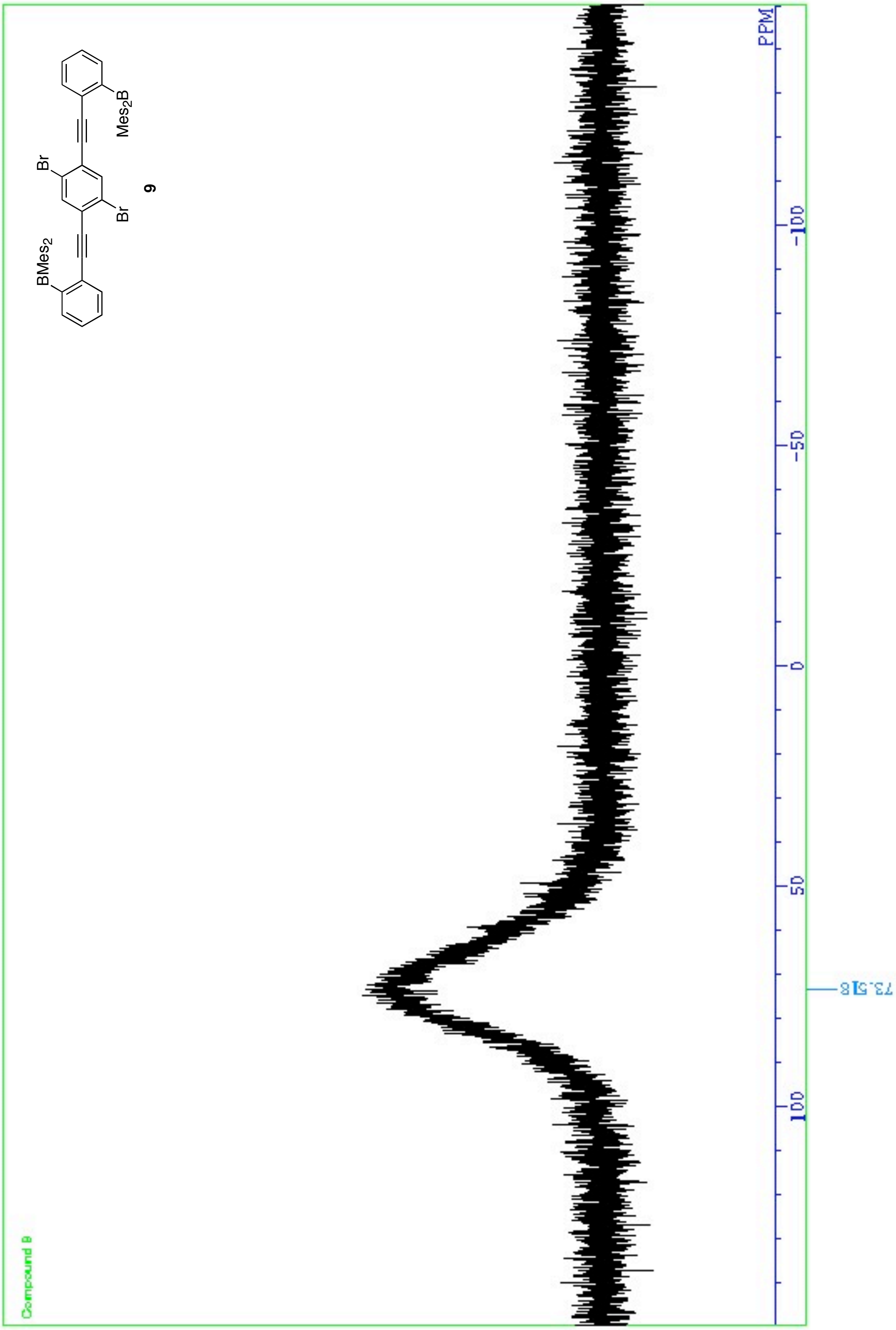


Figure S31. ^{11}B{^{1}H} NMR spectrum of **9** (JEOL AL-400, 128 MHz, CDCl$_3$).

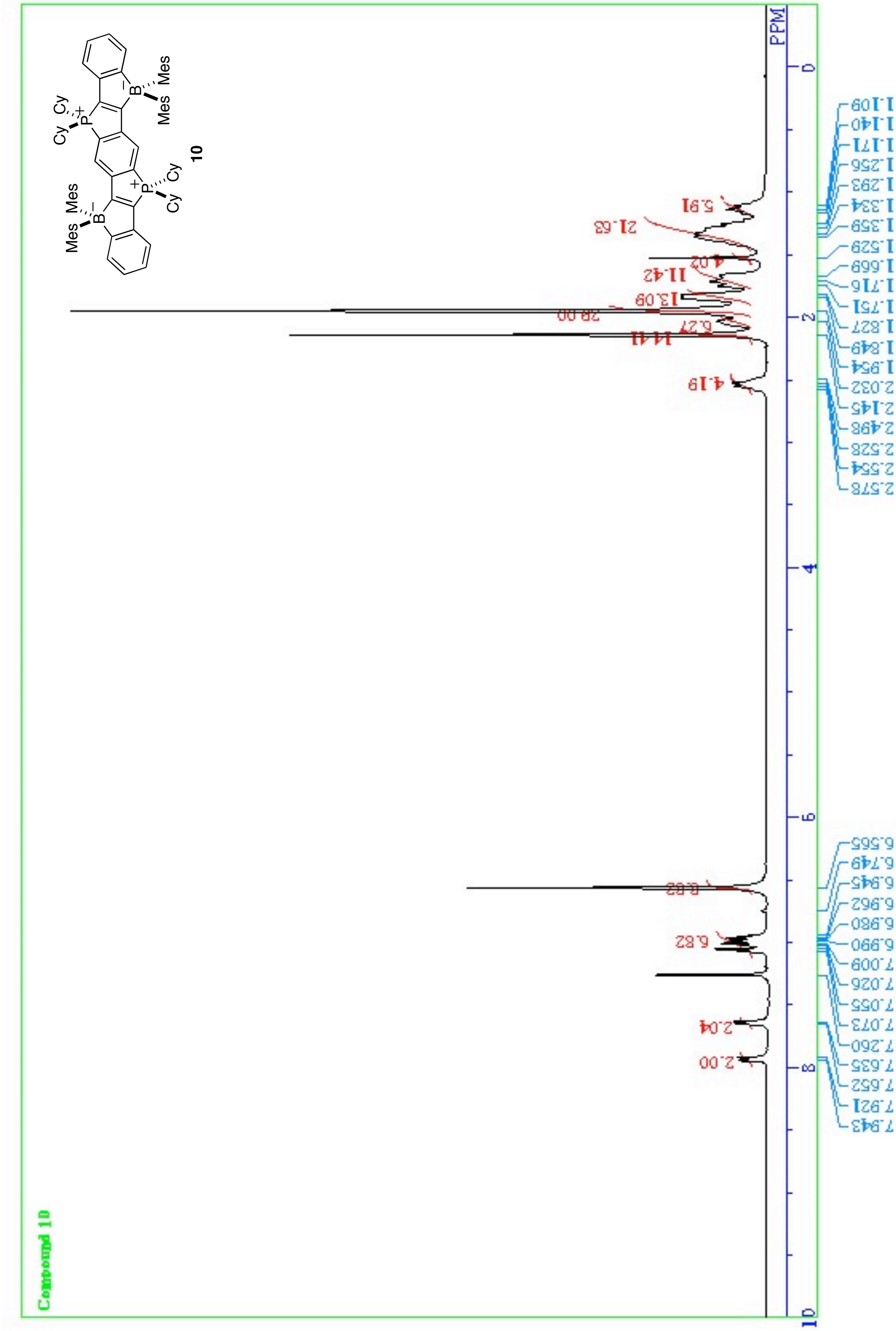


Figure S32. ^{1}H NMR spectrum of **10** (JEOL AL-400, 400 MHz, $CDCl_3$).

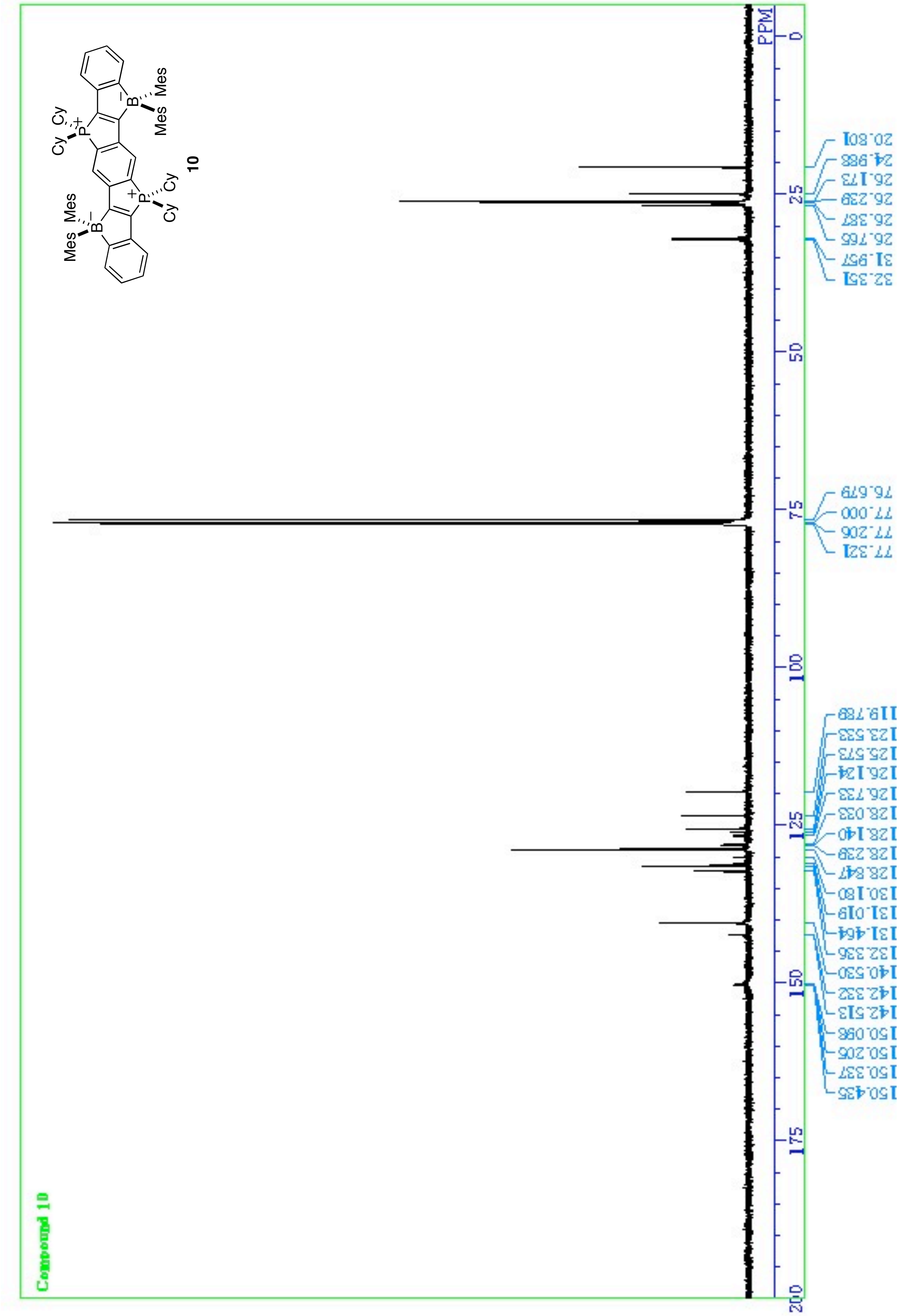


Figure S33. $^{13}C\{^1H\}$ NMR spectrum of **10** (JEOL A-400, 100 MHz, $CDCl_3$).

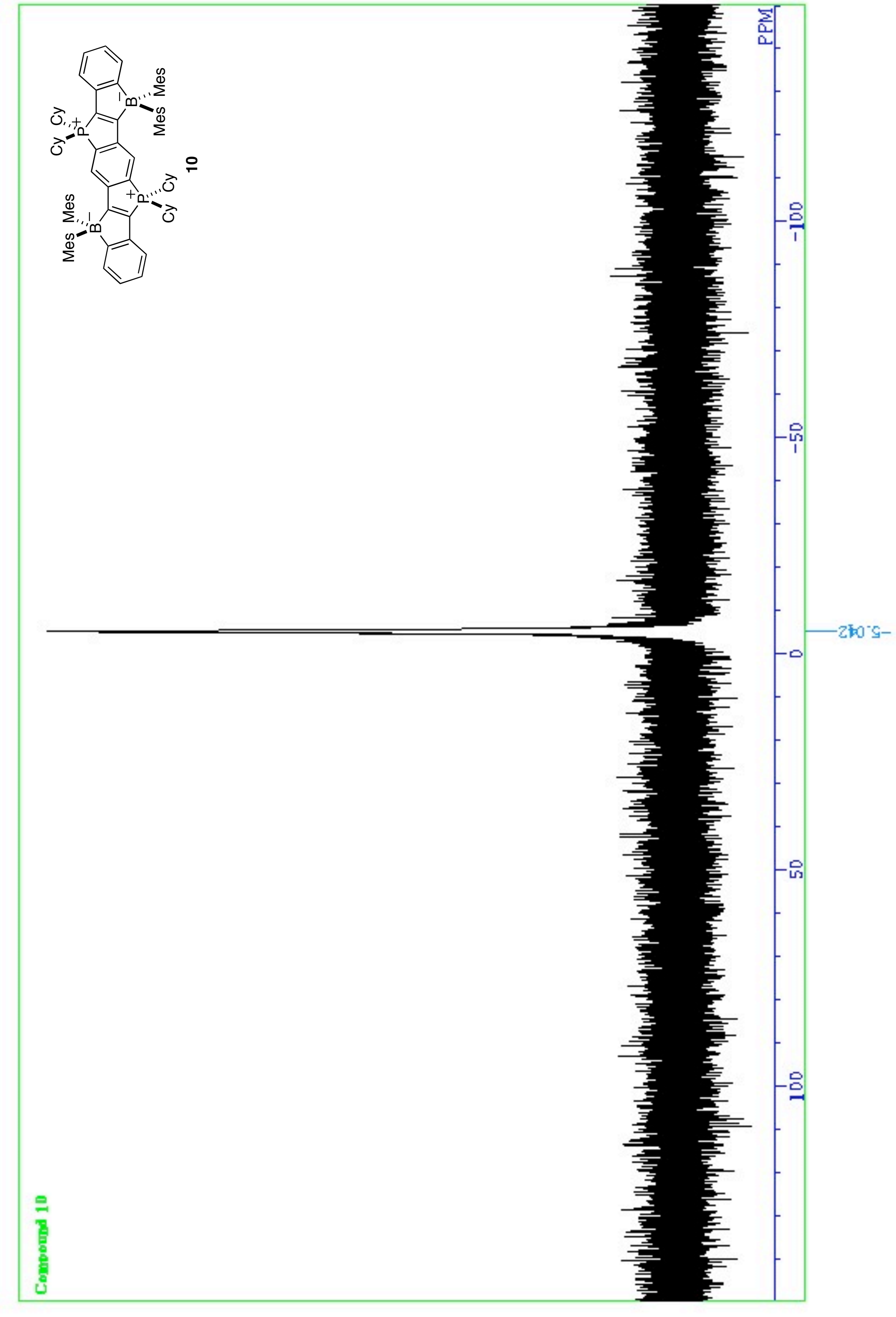


Figure S34. $^{11}B\{^1H\}$ NMR spectrum of **10** (JEOL AL-400, 128 MHz, $CDCl_3$).

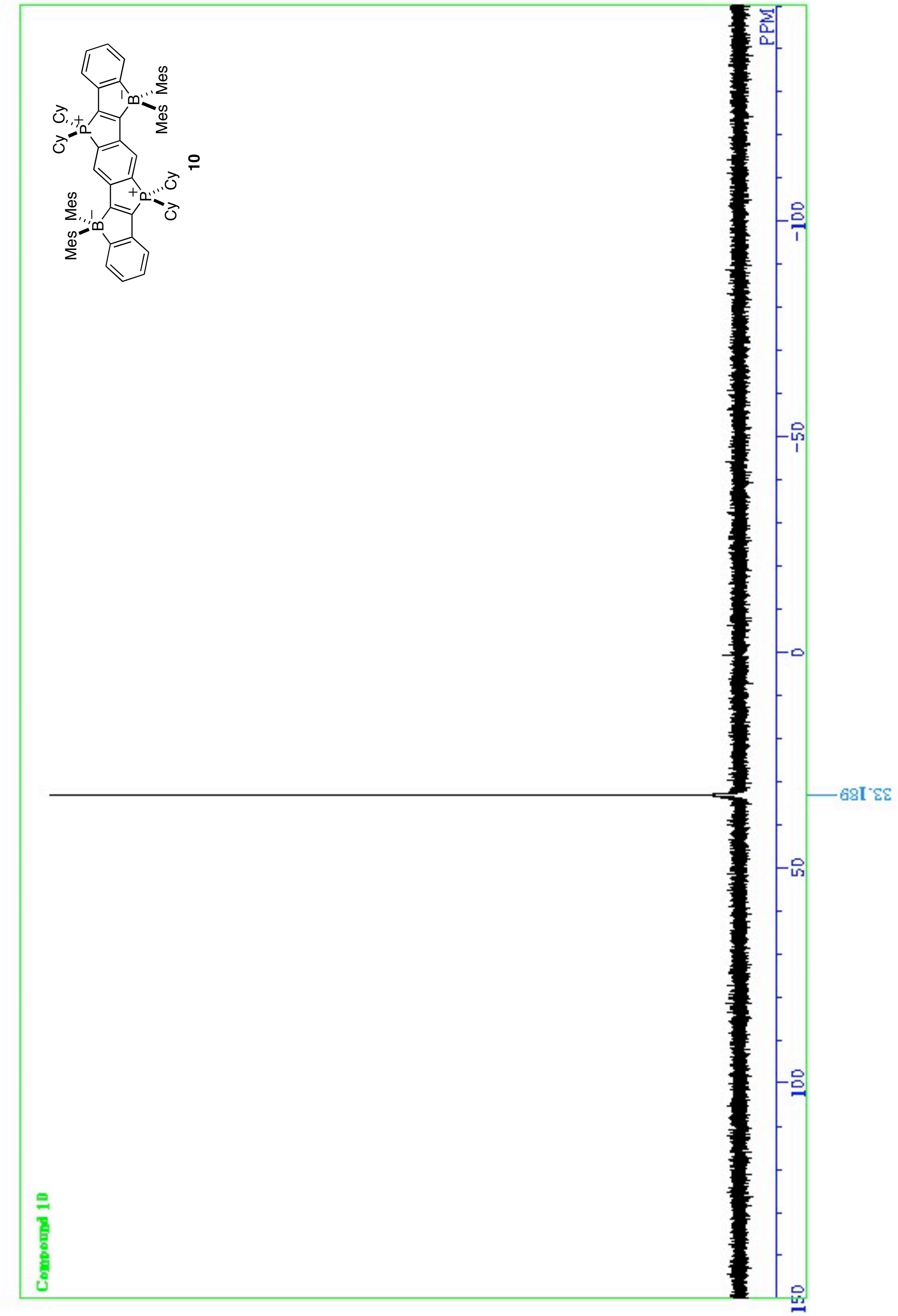


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of **10** (JEOL AL-400, 162 MHz, $CDCl_3$).

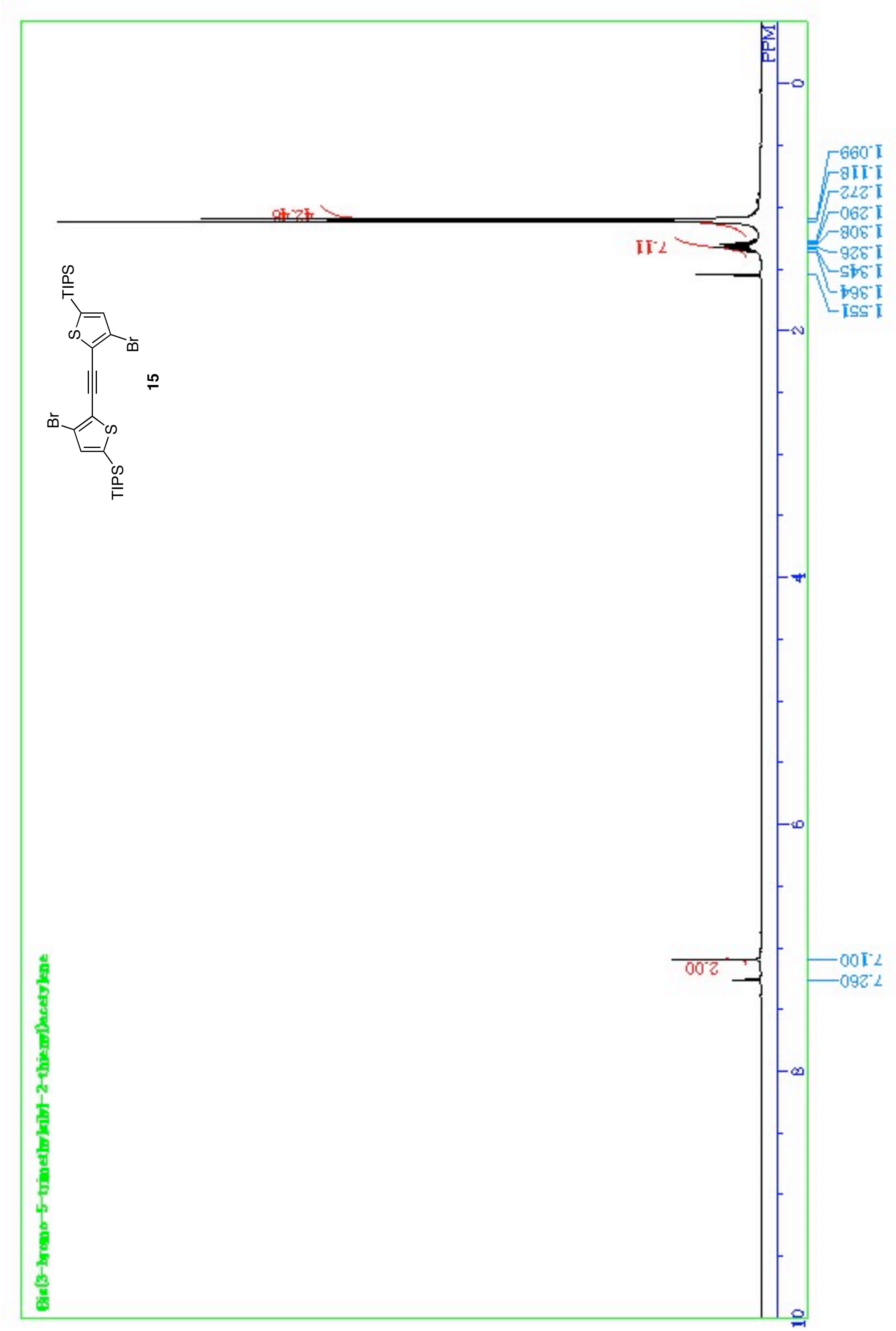


Figure S36. ^{1}H NMR spectrum of **15** (JEOL AL-400, 400 MHz, $CDCl_3$).

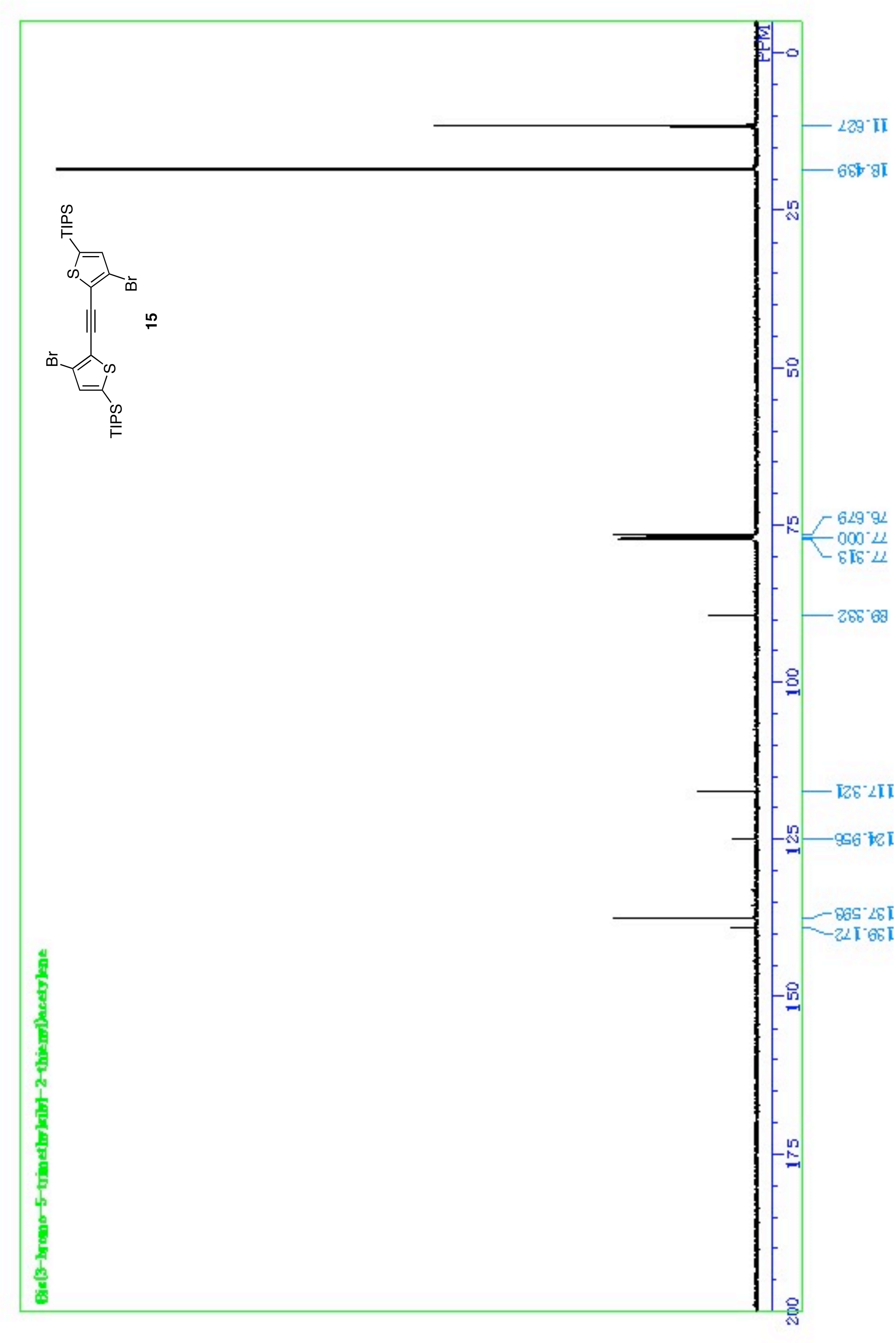


Figure S37. $^{13}C\{^1H\}$ NMR spectrum of **15** (JEOL AL-400, 100 MHz, $CDCl_3$).

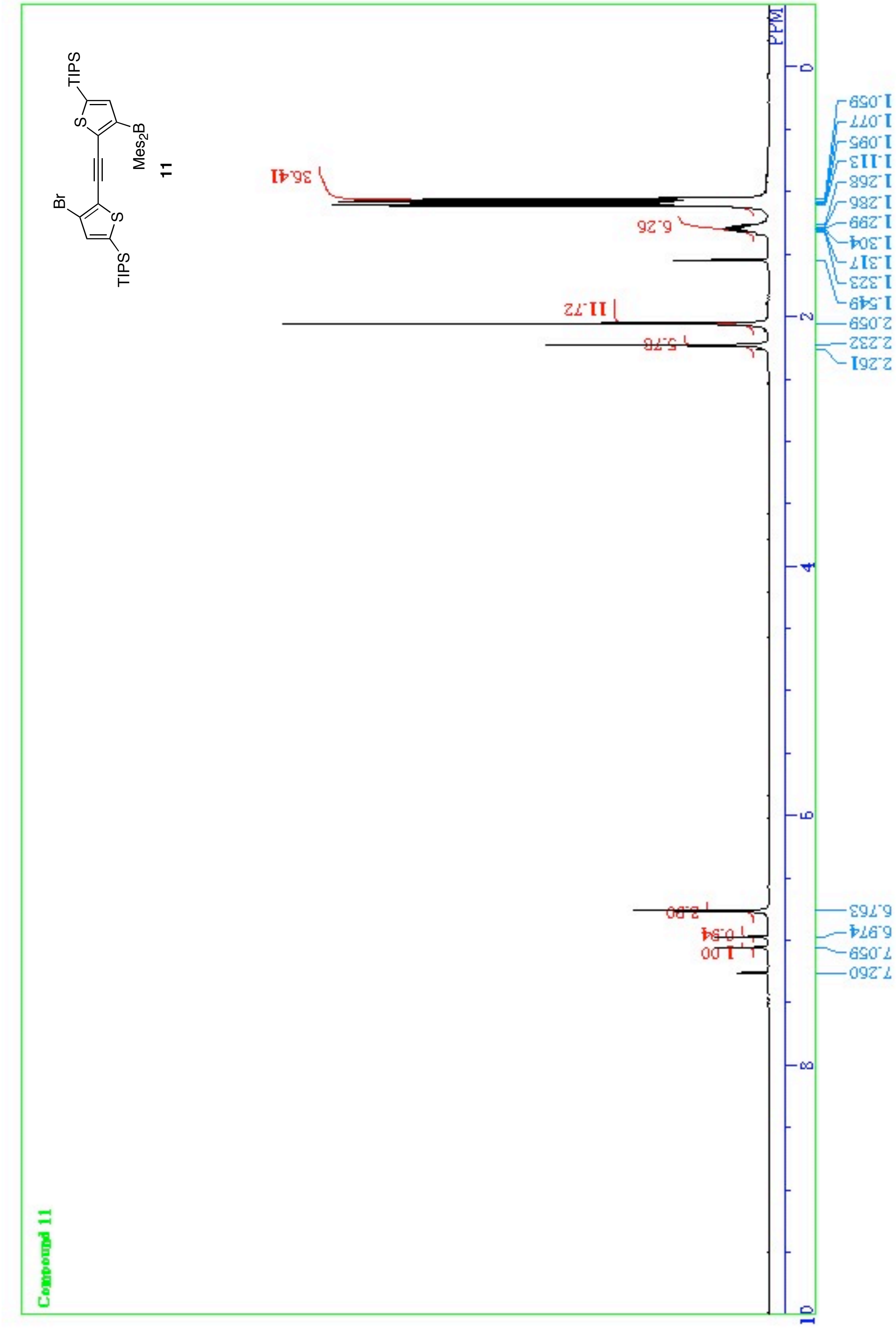


Figure S38. ^{1}H NMR spectrum of **11** (JEOL AL-400, 400 MHz, CDCl$_3$).

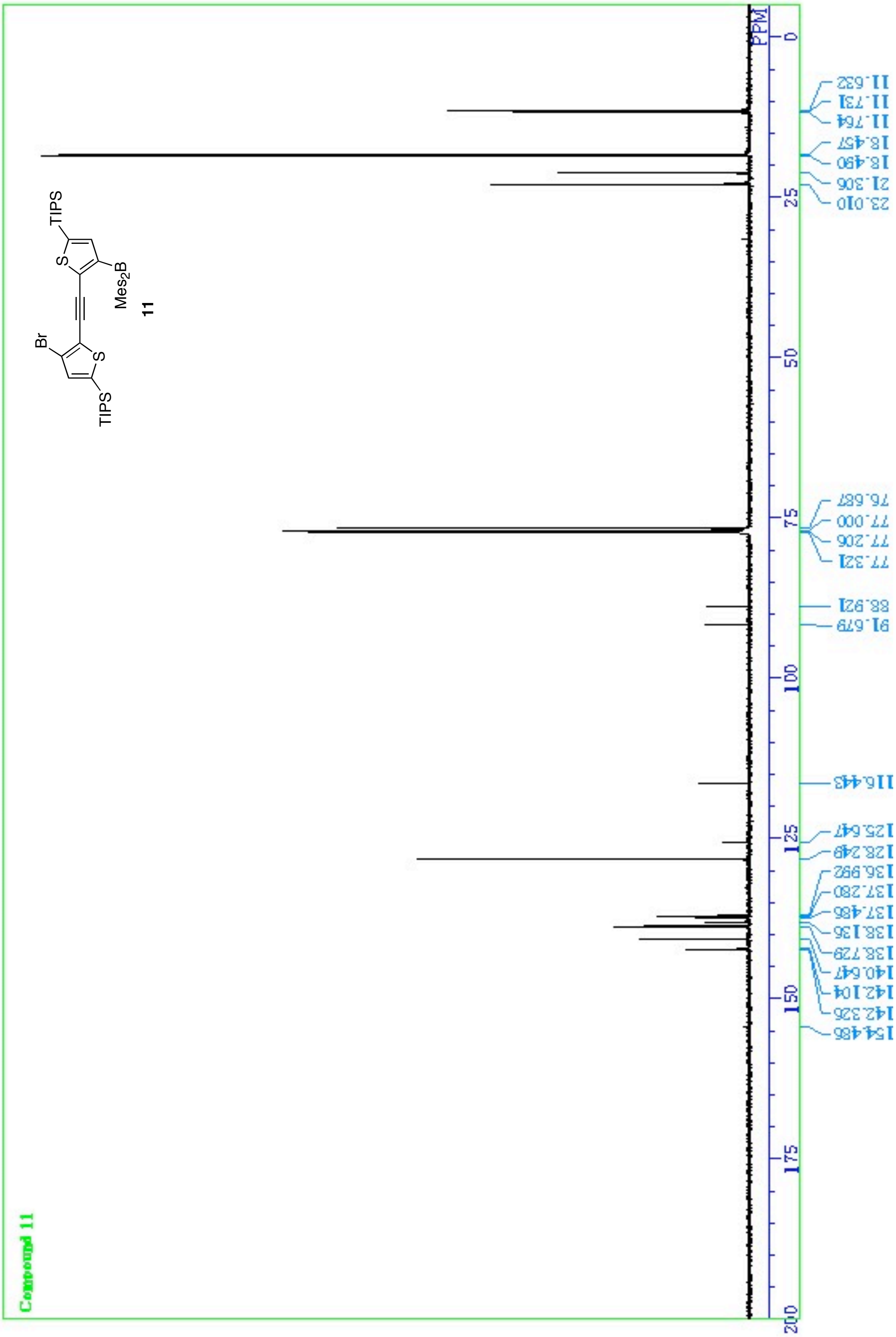


Figure S39. ^{13}C{^{1}H} NMR spectrum of **11** (JEOL AL-400, 100 MHz, CDCl$_3$).

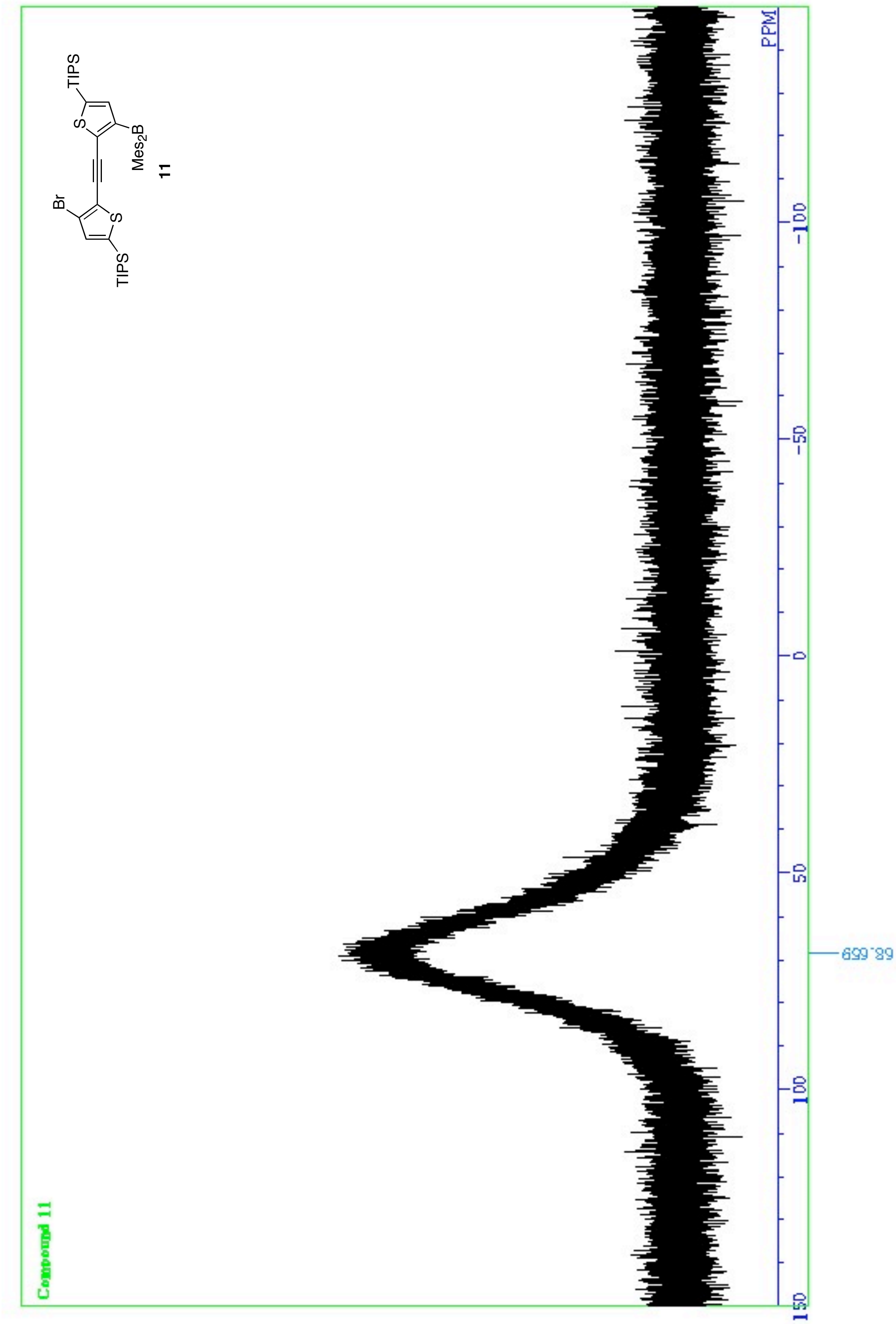


Figure S40. ^{11}B{^{1}H} NMR spectrum of **11** (JEOL AL-400, 128 MHz, CDCl$_3$).

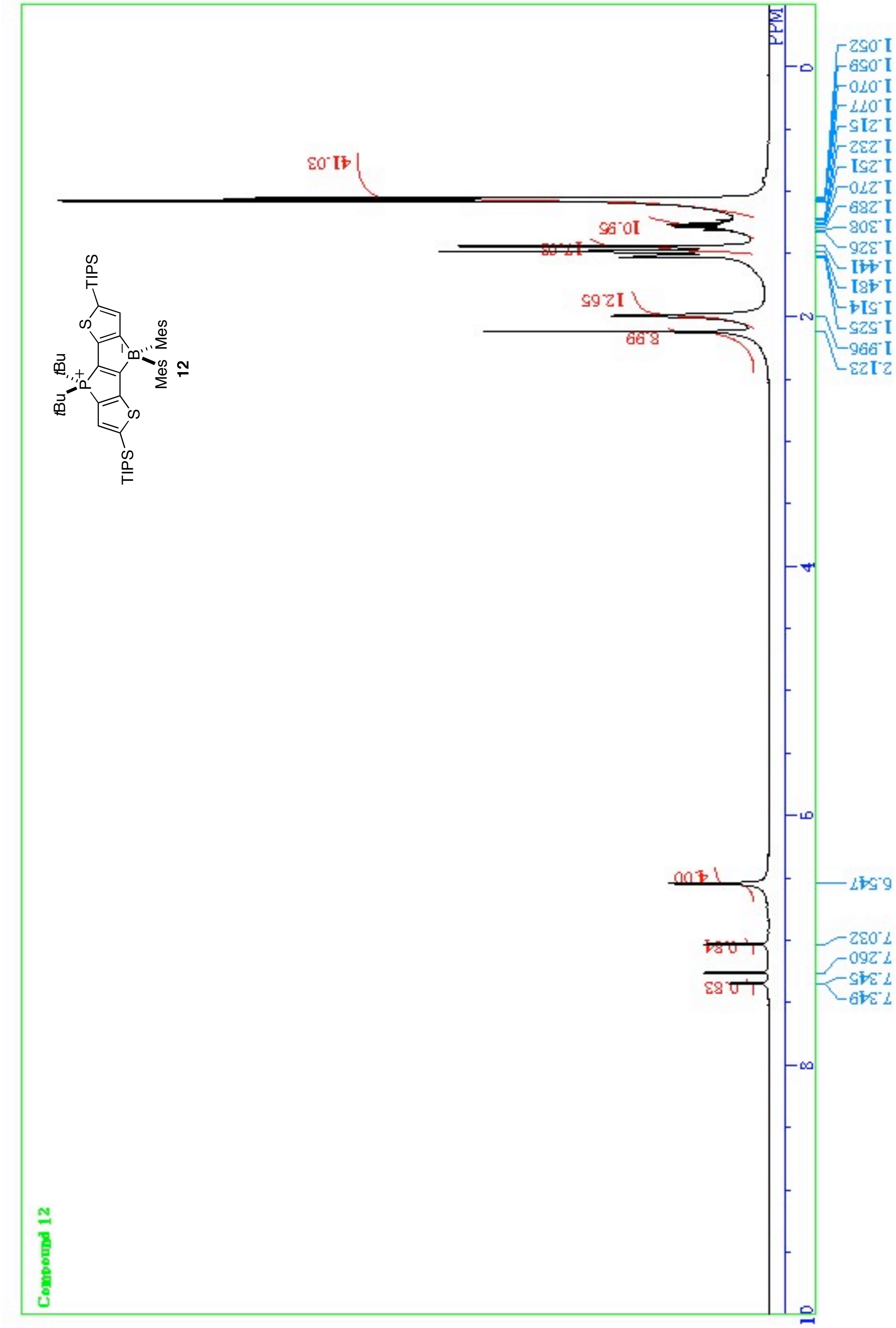


Figure S41. ^{1}H NMR spectrum of **12** (JEOL AL-400, 400 MHz, $CDCl_3$).

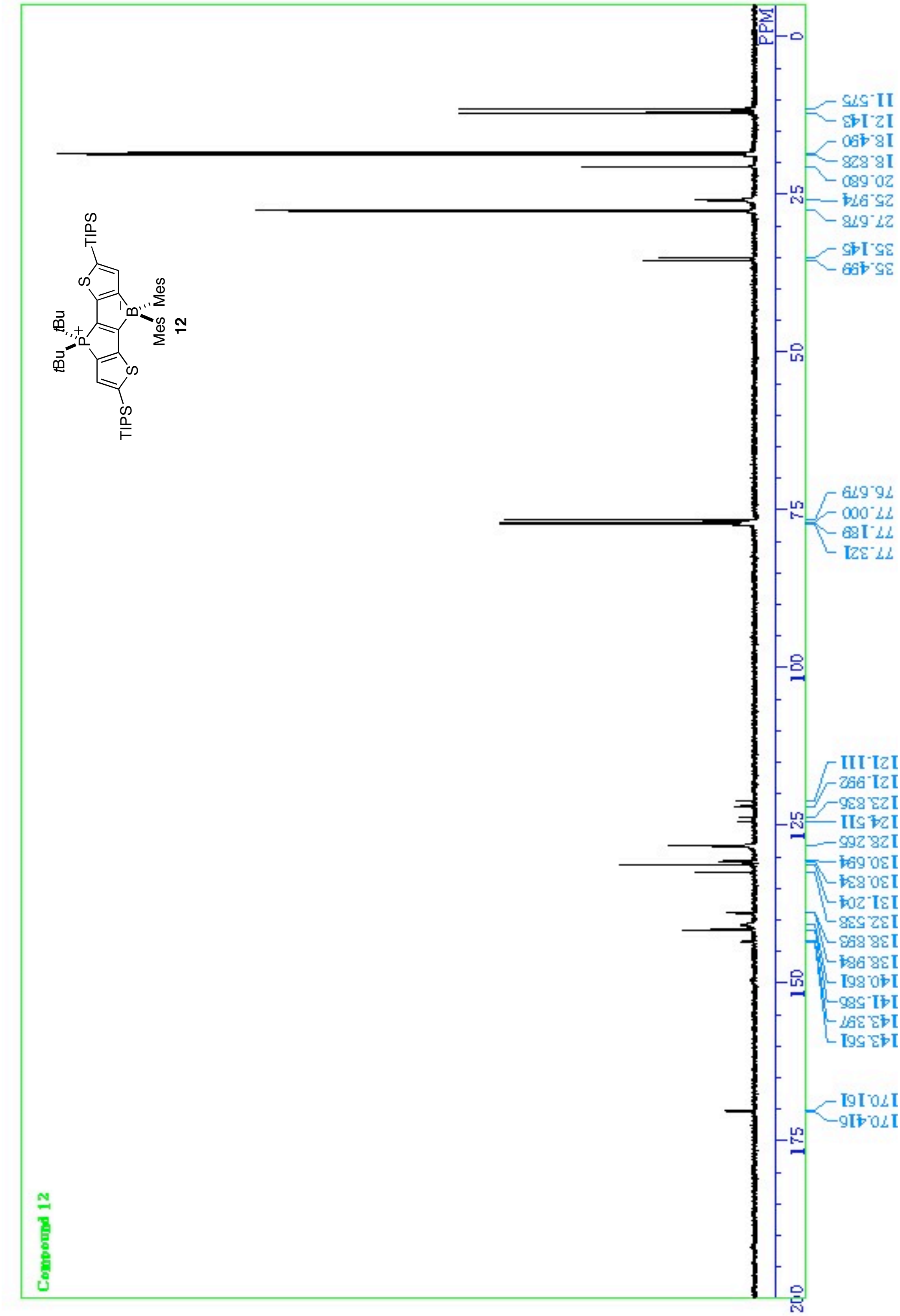


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of **12** (JEOL AL-400, 100 MHz, $CDCl_3$).

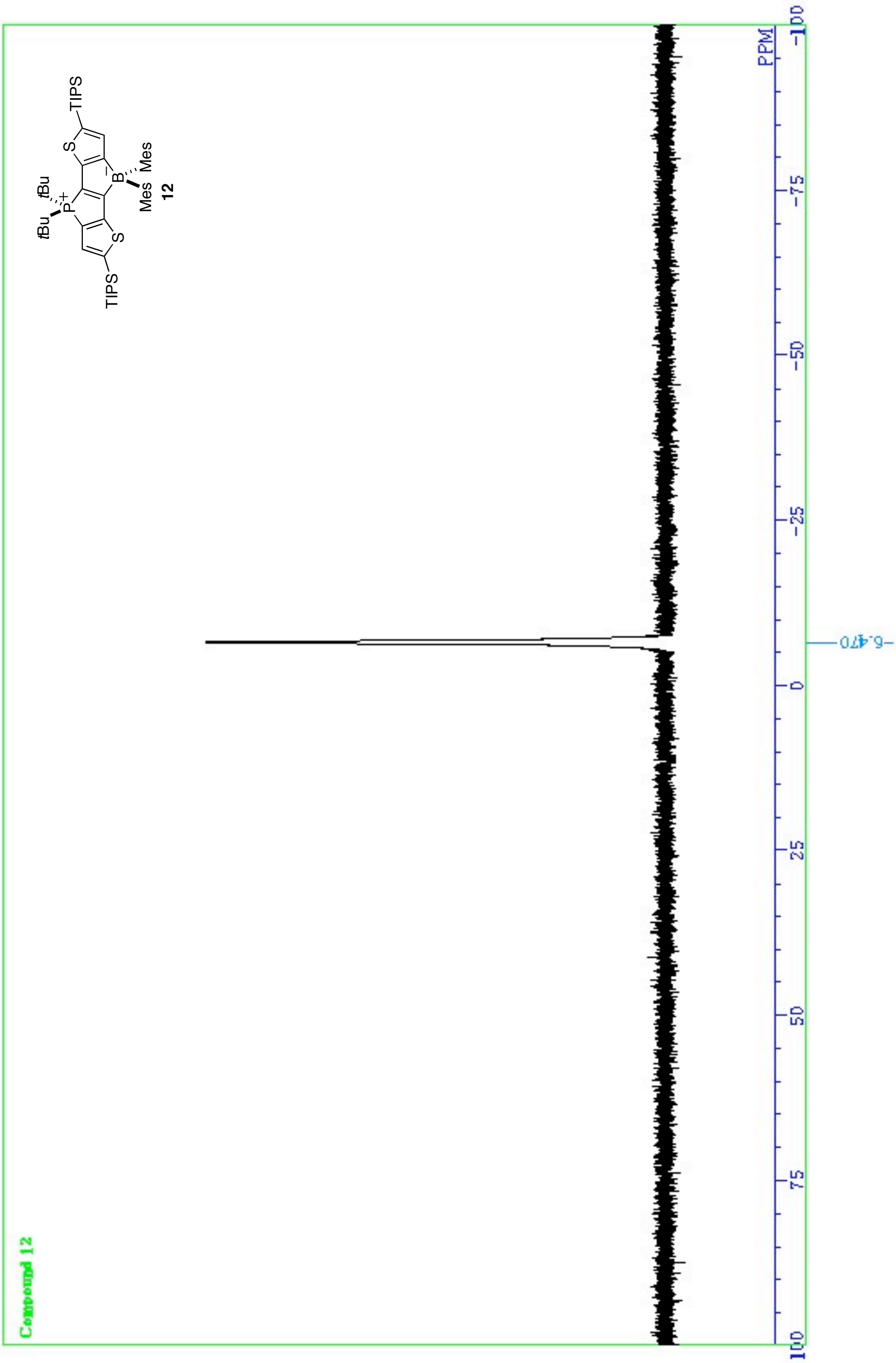


Figure S43. $^{11}B\{^{1}H\}$ NMR spectrum of **12** (JEOL AL-400, 128 MHz, $CDCl_3$).

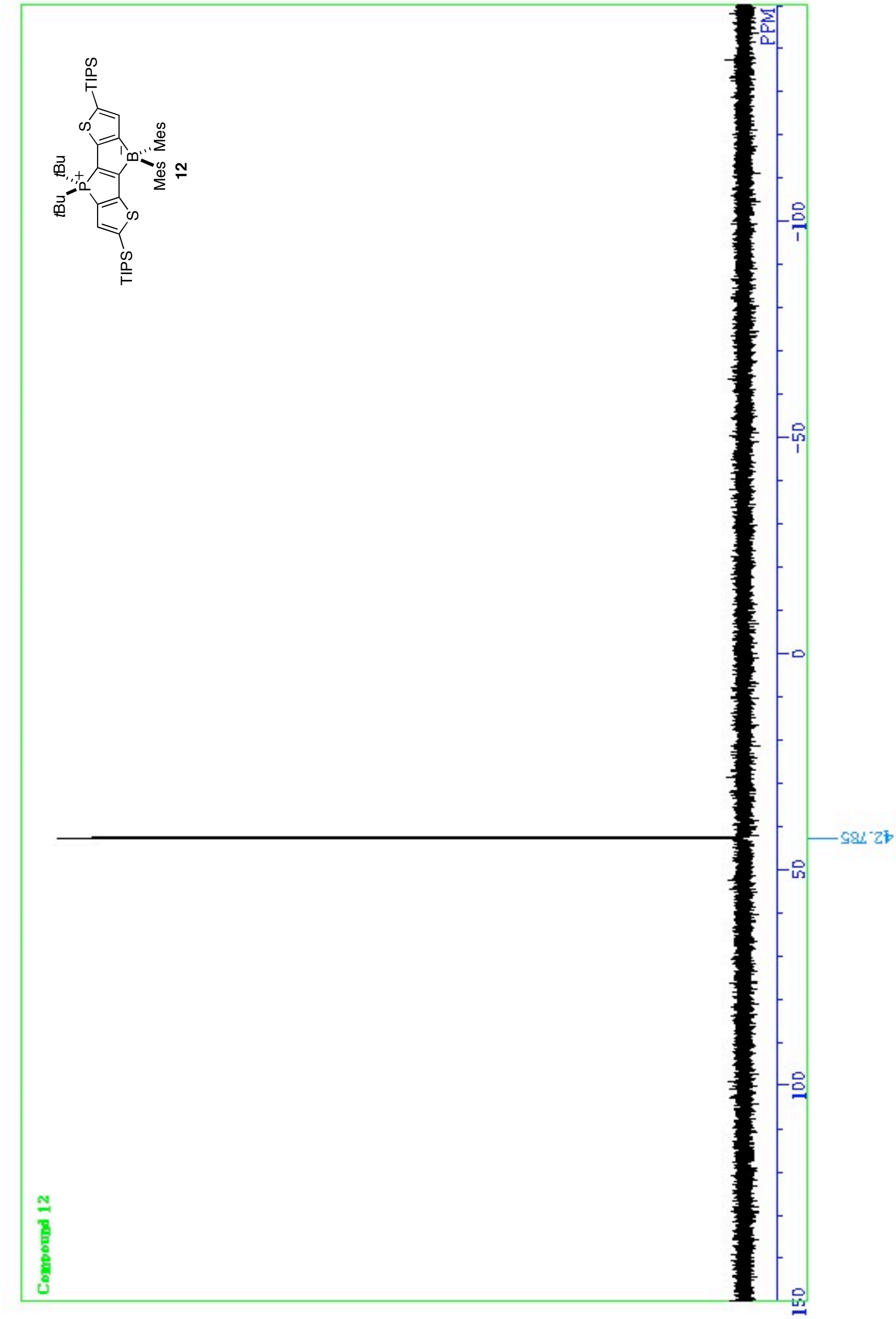


Figure S44. $^{31}P\{^1H\}$ NMR spectrum of **12** (JEOL AL-400, 162 MHz, CDCl$_3$).

3. X-ray crystallographic analysis

X-ray Crystallographic Analysis of 1b. Single crystals of **1b** suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **1b** in dichloromethane. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 21969 reflections were measured at a maximum 2θ angle of 50.0°, of which 6047 were independent reflections (Rint = 0.0689). The structure was solved by direct method (SHELX-97[4]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[4]). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula $C_{40}H_{48}B_2P_2$; FW = 570.56, crystal size 0.20 mm × 0.20 mm × 0.20 mm, monoclinic, $C2/c$, (#15), a = 31.88(10) Å, b = 12.98(2) Å, c = 15.83(3) Å, β = 95.78(3)°, V = 6519(25) Å^3, Z = 8, D_{calcd} = 1.163 g cm^{-3}, μ = 0.111 mm^{-1}; R_1 = 0.0511 ($I > 2\sigma(I)$), wR_2 = 0.1501 (all data), GOF = 1.003.

X-ray Crystallographic Analysis of 10. Single crystals of **10** suitable for X-ray crystallographic analysis were obtained by sl ow diffusion of hexane into a solution of **10** in dichloromethane. Intensity data were collected at 100 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 26892 reflections were measured at a maximum 2θ angle of 50.0°, of which 7236 were independent reflections (Rint = 0.0482). The structure was solved by direct method (SIR97[5]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[4]). Five solvent molecules (CH_2Cl_2) are included in a lattice, two kinds of which are disorderd and solved using appropriate models. Thus, for the first disordered molecules, two sets of CH_2Cl_2 molecules, *i.e.*, (Cl3, C44, Cl4) and (Cl6, C44, Cl8), were placed and their occupancies were refined to be 0.61 and 0.39, respectively. As for the second ones which locate across the lattice, two sets of CH_2Cl_2 molecules were placed, *i.e.*, (Cl5, C43, Cl6*) and (Cl6, C43*, Cl5*), and their occupancies were fixed at 0.5. Two sets of CH_2Cl_2 molecules (Cl5, C43, Cl6*) and (Cl6, C43*, Cl5*) were restrained by ISOR and SIMU instructions during refinement. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula $C_{87}H_{102}B_2Cl_{10}P_2$; FW = 1585.75, crystal size 0.20 mm × 0.20 mm × 0.20 mm, monoclinic, $P2_1/c$, (#14), a = 14.826(16) Å, b = 14.206(16) Å, c = 20.04(2) Å, β = 102.50(3)°, V = 4121(8) Å^3, Z = 2, D_{calcd} = 1.278 g cm^{-3}, μ = 0.421 mm^{-1}; R_1 = 0.0835 ($I > 2\sigma(I)$), wR_2 = 0.1928 (all data), GOF = 1.168.

X-ray Crystallographic Analysis of 12. Single crystals of **12** suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **12** in dichloromethane. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 47465 reflections were measured at a maximum 2θ angle of 50.0°, of which 10390 were independent reflections (Rint = 0.0529). The structure was solved by direct method (SHELX-97[4]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[4]). Four solvent molecules (acetonitrile) are included in a lattice, which are refined isotropically. All other non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula $C_{56}H_{87}BNPS_2Si_2$; FW = 936.35, crystal size 0.20 mm × 0.20 mm × 0.20 mm, monoclinic, $P2_1/a$, (#14), a = 12.650(8) Å, b = 36.12(5) Å, c = 12.482(3) Å, β = 90.98(6)°, V = 5703(9) Å^3, Z = 4, D_{calcd} = 1.091 g cm^{-3}, μ = 0.198 mm^{-1}; R_1 = 0.0820 ($I > 2\sigma(I)$), wR_2 = 0.1713 (all data), GOF = 1.209.

4. Photophysical properties

Measurements. UV-visible absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured with a F-4500 Hitachi spectrometer with a resolution of 1 nm. Dilute solutions in degassed spectral grade solvents in a 1 cm square quartz cell. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system. Fluorescence lifetimes were measured with a Hamamatsu Picosecond Fluorescence Measurement System C4780.

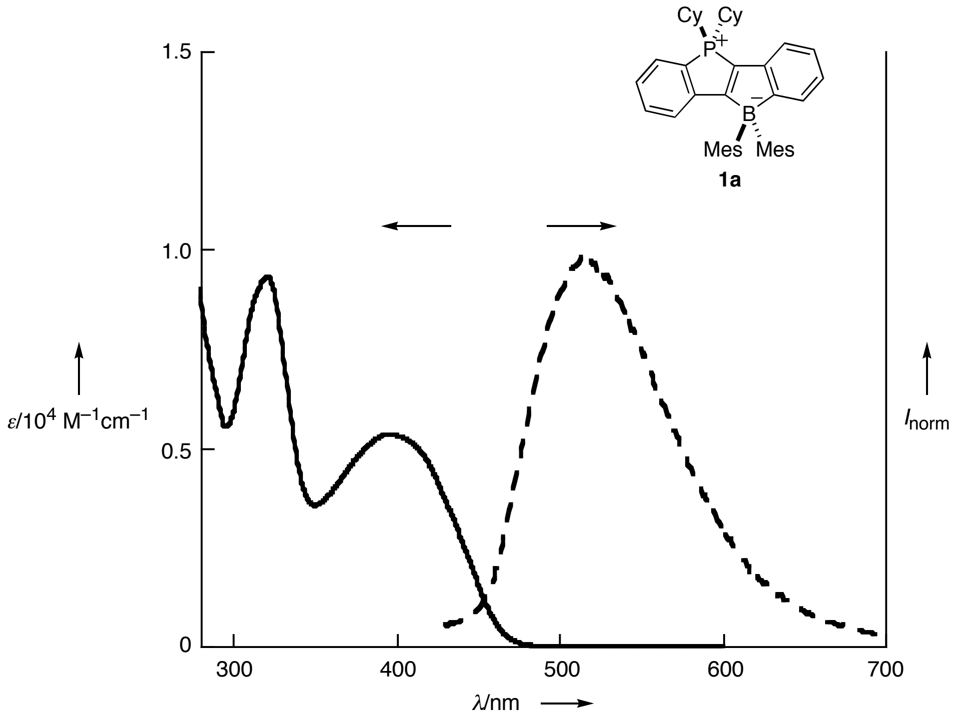


Figure S48. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **1a** in THF. The fluorescence spectrum was obtained upon excitation at 370 nm.

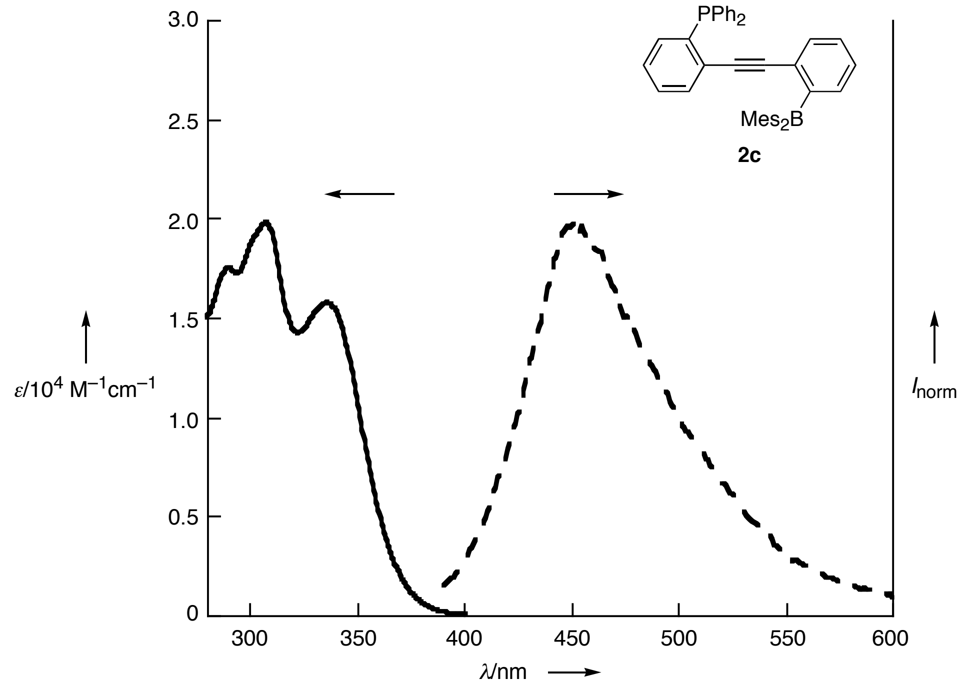


Figure S49. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **2c** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

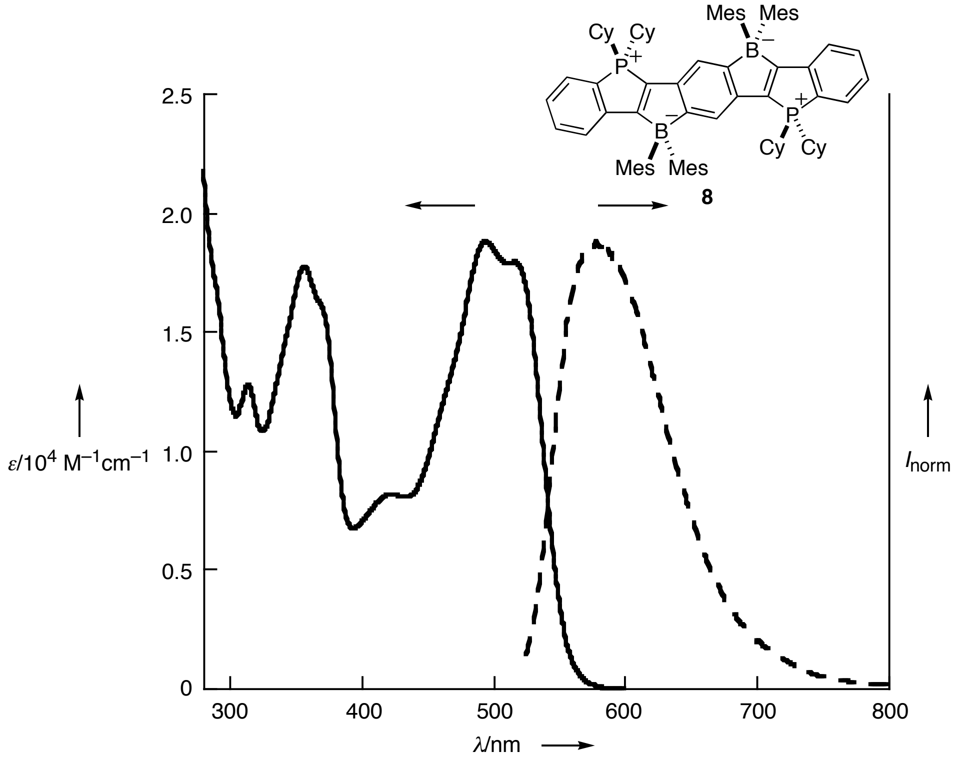


Figure S50. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **8** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

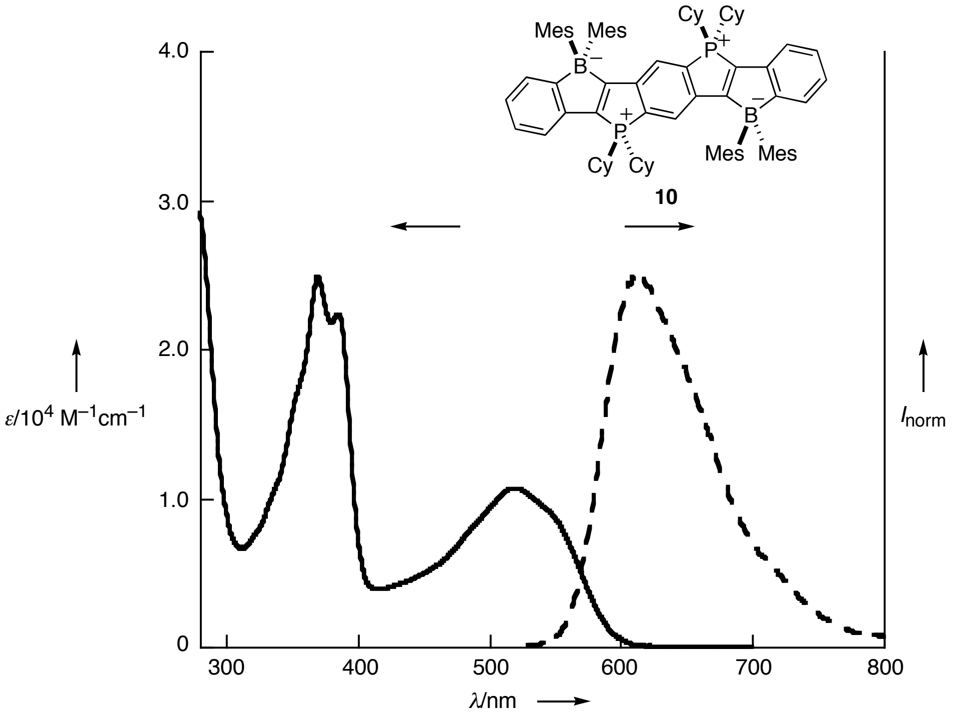


Figure S51. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **10** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

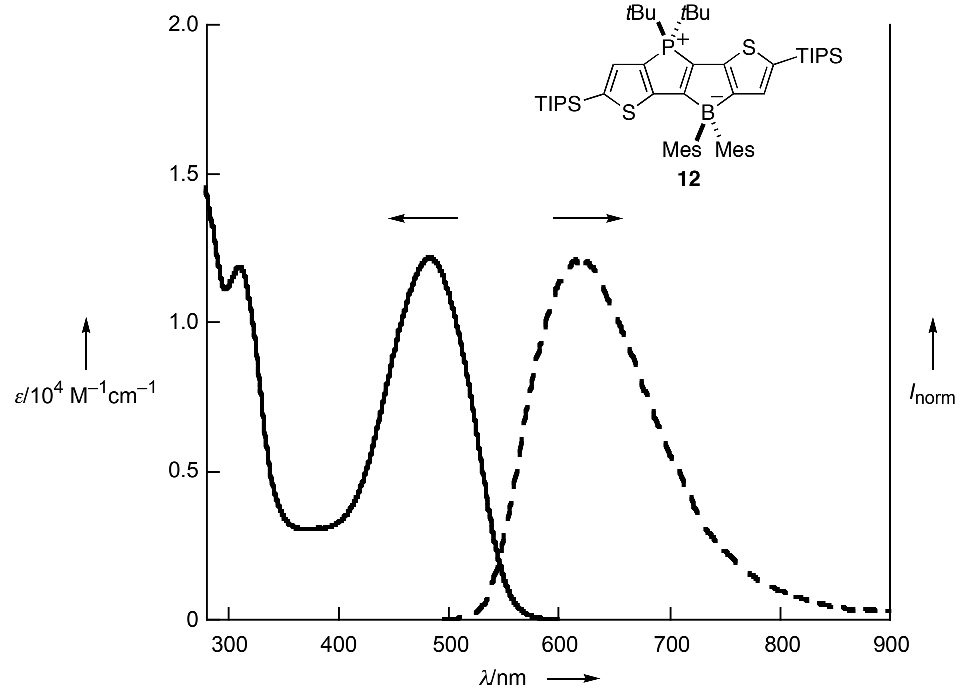


Figure S52. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **12** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

5. Electrochemical properties

Measurements. Cyclic voltammograms were recorded on a CHI600A instrument using degassed solvent under an argon atmosphere. Measurements were performed in CH_2Cl_2 or THF containing $Bu_4N^+PF_6^-$ (0.1 M) with a scan rate of 100 mV s^{-1}. Potentials are determined vs ferrocene/ferrocenium couple.

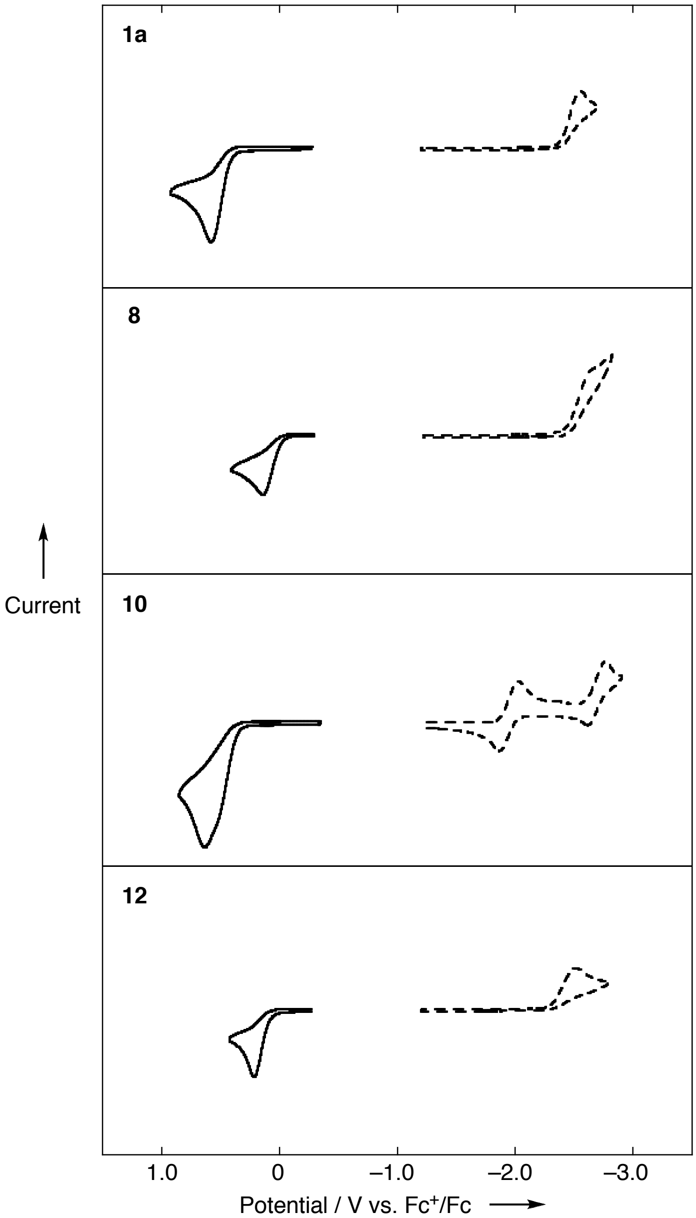
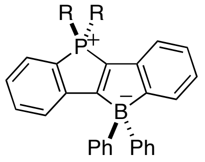
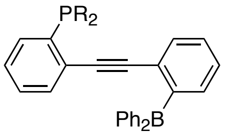


Figure S53. Cyclic voltammograms of **1a**, **8**, **10**, and **12** in CH_2Cl_2 (solid line) or THF (broken line).

6. Theoretical calculation

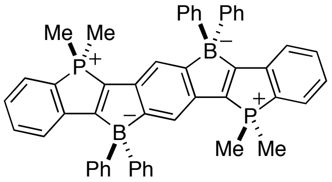


1a′ (R = Me)
1c′ (R = Ph)

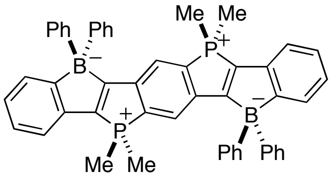


2a′ (R = Me)
2c′ (R = Ph)

The geometry optimizations of model compounds **1a′**, **1c′**, **2a′**, and **2c′** were performed using Gaussian 03 program[6] at the B3LYP/6-31G(d) level. The Cartesian coordinates of these compounds are shown in Tables S1–S4, respectively. The heat of formation of these compounds is summarized in Table S5.



8′



10′

The geometry optimizations and time-dependent DFT calculations of model compounds **8′** and **10′** were performed using Gaussian 98 program[7] at the B3LYP/6-31G(d) level. The Cartesian coordinates of **8′** and **10′** are shown in Tables S6 and S7, respectively. The energy diagram for frontier orbitals are given in Figure S54. The plots of selected molecular orbitals of **8′** and **10′** are also shown in Figure S55 and Figure S56, respectively. The results of TD-DFT calculations are summarized in Table S8.

Table S1. Coordinates (Å) of the Optimized Structure for **1a′** Calculated at the B3LYP/6-31G(d) level

atom	*x*	*y*	*z*
C	-0.781733702	2.861740153	-0.127346274
C	-1.090996968	3.249944626	2.668980906
C	-0.255359559	1.920686377	0.805707823
C	-1.480340277	3.966106883	0.400651512
C	-1.620529697	4.178898852	1.771086031
C	-0.427021867	2.125012935	2.190565323
H	-1.917987980	4.681342797	-0.290722171
H	-2.150033472	5.055110741	2.135799311
H	-0.028333094	1.385927167	2.878821992
H	-1.202708761	3.395400648	3.740327625

(Table S1 continued)

C	1.636203493	-1.574638414	-0.045197003
C	2.983238423	-3.967190994	-0.613066447
C	2.253361381	-1.771977966	-1.295974874
C	1.688316544	-2.602513793	0.937747223
C	2.369649251	-3.785981337	0.628238284
C	2.923468457	-2.958764007	-1.575755075
H	2.206017868	-0.976685328	-2.033076325
H	2.422401997	-4.579198996	1.366746329
H	3.401113406	-3.093499631	-2.542519081
H	3.504177880	-4.897226411	-0.825221032
B	-0.614244409	2.780290843	-1.691869995
P	0.924232734	-2.265328270	2.595921495
C	-1.842598117	3.270006198	-2.570401322
C	-4.053605515	4.140895194	-4.105375455
C	-1.701309004	4.319364567	-3.518386349
C	-3.121815436	2.671714015	-2.409357751
C	-4.200718151	3.103489700	-3.189537113
C	-2.810167272	4.746854319	-4.258745119
H	-5.167824571	2.619565539	-3.071432491
H	-2.690340962	5.561191116	-4.969719220
C	0.740960847	2.318674119	-2.367184930
C	3.152416302	1.604881353	-3.671632395
C	0.748837806	1.347782088	-3.407480007
C	1.978086264	2.911294958	-1.990923875
C	3.157496192	2.555785996	-2.656898960
C	1.951202091	1.000846331	-4.034885224
H	4.091445436	3.033585660	-2.370148589
H	1.939623537	0.252992321	-4.824834200
C	0.968557579	-0.342457114	0.215419972
C	0.412202125	0.722633518	0.411420703
C	-0.380440290	5.026944722	-3.752673739
H	0.370197757	4.356568701	-4.183174571
H	0.045856220	5.429007526	-2.826049994
H	-0.512833128	5.868509080	-4.440294980
C	-3.374578681	1.547516745	-1.421206873
H	-4.279993677	0.994672712	-1.693247631
H	-3.516118349	1.931669393	-0.404234346
H	-2.552116995	0.827151666	-1.373450412
C	-0.507685615	0.623794711	-3.848480080
H	-0.981227504	0.090583683	-3.015581835

(Table S1 continued)			
H	-0.273316594	-0.119481650	-4.617364803
H	-1.254676487	1.308923331	-4.259852450
C	2.093623423	3.949124638	-0.889915449
H	2.034023399	3.487879745	0.102138414
H	1.306945724	4.708572390	-0.932717353
H	3.056094418	4.467090897	-0.954928568
C	-0.872030799	-2.601814866	2.285528027
C	-3.639633255	-3.004131950	1.968040513
C	-1.371135753	-3.295191338	1.172601513
C	-1.784573639	-2.105609692	3.231012327
C	-3.155721187	-2.311533246	3.079675059
C	-2.744640544	-3.491457067	1.014215663
H	-0.684600929	-3.679200069	0.423894620
H	-1.416904834	-1.549293774	4.090343146
H	-3.846211141	-1.922390585	3.823529439
H	-3.114706556	-4.027830716	0.143963336
H	-4.708320582	-3.157632515	1.842863694
C	1.443597995	-3.749504282	3.580306294
C	2.365520090	-5.874311155	5.181222933
C	0.714881426	-4.945518408	3.671784487
C	2.635823766	-3.633691735	4.315270399
C	3.099208883	-4.689023803	5.101025106
C	1.171600918	-5.997636177	4.468336532
H	-0.215369770	-5.054777560	3.122372269
H	3.201846912	-2.705742153	4.273931472
H	4.025915218	-4.581486446	5.658885004
H	0.592886079	-6.915900018	4.530442507
H	2.718626087	-6.694354417	5.801049123
H	-4.902082395	4.473490737	-4.698262651
H	4.076559323	1.337660332	-4.178221920

Table S2. Coordinates (Å) of the Optimized Structure for **1c′** Calculated at the B3LYP/6-31G(d) level

atom	*x*	*y*	*z*
C	-0.333141373	-0.123144705	0.513923522
C	0.682066112	0.032490649	-0.397342210
C	0.222804693	0.262091946	-1.777601451
C	-0.976214827	0.655515448	-4.297686491
C	-1.188337739	0.278241713	-1.939906344

(Table S2 continued)

C	1.018375331	0.452135320	-2.910714964
C	0.413280805	0.648016759	-4.157408372
C	-1.794041358	0.466185440	-3.175066565
H	1.038845692	0.795723902	-5.033612039
H	-2.875966957	0.469103154	-3.280132605
H	-1.426349575	0.806773197	-5.274322898
C	0.114767122	-0.331225390	1.889506377
C	1.424259536	-0.695237058	4.298891080
C	1.536529056	-0.289890183	1.900155075
C	-0.640829346	-0.548394136	3.046619629
C	0.026845784	-0.729515443	4.259564679
C	2.167282489	-0.479515617	3.130519186
H	-0.540628774	-0.897611094	5.171658293
H	3.253822874	-0.462569124	3.188615821
H	1.937138104	-0.838274212	5.247531534
H	2.098067283	0.452039821	-2.812024692
H	-1.729364726	-0.573424493	3.014865647
P	-1.912121065	-0.004735816	-0.303576615
B	2.129690301	-0.032488762	0.385426739
C	3.074625737	-1.279283623	-0.086811320
C	4.743893662	-3.493292703	-0.753462377
C	2.619294860	-2.341704648	-0.889252121
C	4.406290703	-1.373968306	0.366681499
C	5.228251765	-2.455273588	0.046249410
C	3.431712068	-3.430046542	-1.221559746
H	1.598380866	-2.325770285	-1.267657414
H	4.812838334	-0.571121957	0.978595078
H	6.250559075	-2.486924456	0.418258743
H	3.038060563	-4.228313441	-1.848428697
H	5.381658005	-4.336478453	-1.009051237
C	2.841261482	1.440919126	0.207389811
C	3.974686006	4.026322986	-0.182594078
C	2.453466800	2.548866302	0.985702869
C	3.820448621	1.684156429	-0.774850857
C	4.381303186	2.949091309	-0.970992932
C	3.005205879	3.818141027	0.800777106
H	1.706551998	2.411216659	1.764889552
H	4.171245918	0.856226084	-1.387593845
H	5.142134965	3.090780860	-1.736460935
H	2.682286644	4.645767216	1.429913687

(Table S2 continued)

H	4.411011143	5.012138853	-0.327605825
C	-2.984597987	1.378233002	0.189768718
C	-4.502984529	3.558219889	1.059703971
C	-2.776405853	2.649183951	-0.369550995
C	-3.952672004	1.207348615	1.192388378
C	-4.708787570	2.296875937	1.622213701
C	-3.537216602	3.732834861	0.066475487
H	-2.024555101	2.789836754	-1.139602825
H	-4.120261275	0.228750598	1.631869649
H	-5.457161422	2.159464721	2.397296089
H	-3.373584764	4.713484279	-0.370575166
H	-5.093813690	4.405217979	1.396853059
C	-2.875685098	-1.543037284	-0.224885260
C	-4.278470417	-3.957997015	-0.195841913
C	-4.176063392	-1.607831580	-0.753174554
C	-2.282090108	-2.691961375	0.320068942
C	-2.988583343	-3.895379119	0.332544765
C	-4.872066320	-2.814608890	-0.737986611
H	-4.647682147	-0.719966377	-1.165260549
H	-1.280862387	-2.642618585	0.736193958
H	-2.528021649	-4.781739982	0.758572143
H	-5.877110288	-2.862547860	-1.147218651
H	-4.824657211	-4.897063727	-0.183780601

Table S3. Coordinates (Å) of the Optimized Structure for **2a′** Calculated at the B3LYP/6-31G(d) level

atom	*x*	*y*	*z*
C	-0.743371562	2.058264236	1.054070453
C	0.547197341	2.651781912	3.511207124
C	0.237430825	1.178315786	1.597408149
C	-1.055110251	3.212455004	1.797319079
C	-0.412332872	3.524912200	2.995245701
C	0.859762701	1.482628100	2.825317860
H	-1.818115606	3.887388000	1.417839036
H	-0.668755973	4.435966647	3.529440933
H	1.583933052	0.783258961	3.232258639
H	1.043684729	2.874721653	4.451993626
C	1.235248158	-2.365373537	-0.135037750
C	1.773369626	-4.813612721	-1.386331321

(Table S3 continued)

C	0.602542373	-2.709064639	-1.346086984
C	2.177662746	-3.256082365	0.450853211
C	2.418566572	-4.475388461	-0.194841639
C	0.868212205	-3.924871352	-1.967013067
H	-0.096738607	-2.004646078	-1.785768834
H	3.123906269	-5.181760466	0.230571129
H	0.368024512	-4.178487462	-2.897708212
H	1.984375060	-5.768534904	-1.860783670
B	-1.470709646	1.833676085	-0.326668986
P	2.959398152	-2.787679626	2.067774019
C	-3.031610857	1.969413594	-0.375809970
C	-5.853352820	2.211562613	-0.428038598
C	-3.822607464	1.633931216	0.745408356
C	-3.710768992	2.440783374	-1.521138973
C	-5.098458298	2.572726775	-1.546337874
C	-5.212315547	1.736043718	0.718424127
H	-5.592298111	2.954019865	-2.436622282
H	-5.795666253	1.453899909	1.591230317
C	-0.642812451	1.564607541	-1.627806453
C	0.864840953	1.128746921	-3.985362042
C	0.668803889	2.066807980	-1.767894392
C	-1.168213555	0.830127269	-2.713735099
C	-0.423894302	0.602112257	-3.871073279
C	1.408239320	1.868066143	-2.932107870
H	-0.849243396	0.021370660	-4.685881641
H	2.410981201	2.279261433	-3.016533556
C	4.144333863	-4.198266321	2.357579093
C	4.186925923	-1.500996415	1.483044004
C	0.904815008	-1.121222535	0.478131148
C	0.583141152	-0.049821106	0.958502089
H	-3.334196003	1.277346295	1.648143990
H	-3.136271744	2.724917163	-2.398316477
H	-6.936456355	2.304253827	-0.448448818
H	1.443956986	0.961503557	-4.890152291
H	-2.171953739	0.420258043	-2.640485199
H	1.109300565	2.629482256	-0.949034946
H	3.596387242	-5.115201650	2.597279343
H	4.818427409	-4.392365029	1.515042281
H	4.751711852	-3.941457142	3.232393571
H	3.645827639	-0.622390945	1.121926663

(Table S3 continued)

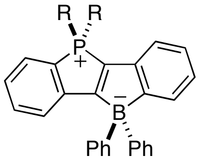
H	4.808114051	-1.194017813	2.332043057
H	4.836179095	-1.873495948	0.682937497

Table S4. Coordinates (Å) of the Optimized Structure for **2c′** Calculated at the B3LYP/6-31G(d) level

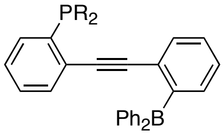
atom	*x*	*y*	*z*
C	-0.863987249	2.543378330	-2.062757692
C	-2.263223819	3.865452572	0.022077404
C	-0.985507732	1.952005439	-0.771824322
C	-1.441260845	3.814298598	-2.245496719
C	-2.147096565	4.464963202	-1.233311452
C	-1.676828417	2.625528607	0.255477454
H	-1.341036104	4.299313939	-3.213191119
H	-2.594189312	5.437822867	-1.420212807
H	-1.747256977	2.158395740	1.233129918
H	-2.802053125	4.366439530	0.822103692
C	0.710624910	-1.611073765	0.217134237
C	1.842937519	-4.111307762	0.789099972
C	1.006357269	-2.520215426	-0.817718527
C	0.981394980	-1.966945289	1.568015027
C	1.548324953	-3.221612702	1.824339495
C	1.570547311	-3.759758087	-0.533486534
H	0.785017311	-2.234613903	-1.841388142
H	1.765461608	-3.510087946	2.847501384
H	1.797202578	-4.448426837	-1.342996198
H	2.282134574	-5.078400858	1.019741217
B	-0.166049022	1.850758801	-3.294809195
P	0.688749600	-0.693006493	2.885496297
C	-0.571112692	0.399451651	-3.723007755
C	-1.348155545	-2.204503308	-4.522342408
C	-1.868218962	-0.094669402	-3.466862100
C	0.324848246	-0.464883003	-4.389435029
C	-0.050089538	-1.752503509	-4.773664342
C	-2.259610375	-1.369376203	-3.871715556
H	0.664916873	-2.400250466	-5.275104074
H	-3.270005453	-1.717090992	-3.672165476
C	0.869486844	2.678786445	-4.130624304
C	2.740294569	4.200074203	-5.616979592
C	1.660439356	3.677509248	-3.520420626

(Table S4 continued)			
C	1.046638893	2.479882514	-5.517768235
C	1.957918683	3.234784691	-6.254906276
C	2.593531857	4.417155966	-4.244848395
H	2.061034242	3.070201563	-7.324564066
H	3.200399673	5.167290674	-3.744132147
C	0.131306194	-0.352395096	-0.117580215
C	-0.379294207	0.698474376	-0.458341700
C	-1.151317841	-0.744518729	3.111032231
C	-3.932529723	-0.641536830	3.537020430
C	-1.729624088	0.308376216	3.840520441
C	-1.992009579	-1.739848386	2.591593421
C	-3.371900800	-1.686210057	2.800903143
C	-3.106624563	0.356155144	4.059614071
H	-1.094184881	1.096145727	4.239453332
H	-1.568505238	-2.557520441	2.015967649
H	-4.008970791	-2.464425710	2.388047838
H	-3.534933828	1.175375390	4.631620696
H	-5.006551144	-0.601807656	3.698727856
C	1.284048636	-1.556798858	4.416199676
C	2.340203967	-2.736633240	6.743496856
C	0.507715864	-2.433806168	5.190163182
C	2.594698190	-1.274395128	4.835375397
C	3.122792503	-1.865047498	5.984161810
C	1.031320005	-3.016770658	6.345366428
H	-0.511902515	-2.657799346	4.890855765
H	3.202498155	-0.581073743	4.258519962
H	4.140100755	-1.636271822	6.291213378
H	0.415514067	-3.691270785	6.935119861
H	2.745596788	-3.190494824	7.644094815
H	0.445186164	1.732207513	-6.027182161
H	3.458802988	4.783480009	-6.187562892
H	1.544708750	3.865569164	-2.456491130
H	-2.581559634	0.538497324	-2.946158197
H	-1.647063538	-3.203465921	-4.830373769
H	1.336409867	-0.125243383	-4.593967032

Table S5. The Heat of Formation of Model Compounds **1a′**, **1c′**, **2a′**, and **2c′**[a]



1a′ (R = Me)
1c′ (R = Ph)



2a′ (R = Me)
2c′ (R = Ph)

	ΔH°_{f} / kcal mol^{-1}
1a′	-908359.8877
2a′	-908349.8356
1c′	-1148976.893
2c′	-1148967.289

[a] Calculated at the B3LYP/6-31G(d) level.

Table S6. Coordinates (Å) of the Optimized Structure for **8′** Calculated at the B3LYP/6-31G(d) level

atom	*x*	*y*	*z*
C	-0.3909	-0.1758	-1.3684
C	0.2709	0.1683	1.4108
C	-0.2086	-1.2672	-0.4722
C	-0.2201	1.1004	-0.8461
C	0.1079	1.2574	0.5086
C	0.1008	-1.1091	0.8881
H	-0.3368	1.9710	-1.4945
H	0.2203	-1.9798	1.5365
C	-0.3892	-2.4951	-1.2299
C	-0.6616	-2.3203	-2.5665
C	-0.8719	-3.5770	-3.3003
C	-1.2089	-6.1483	-4.4133
C	-1.1668	-3.7235	-4.6588
C	-0.7532	-4.7581	-2.5156
C	-0.9144	-6.0291	-3.0489
C	-1.3326	-5.0019	-5.2006
H	-1.2689	-2.8415	-5.2807
H	-0.8187	-6.9194	-2.4315
B	-0.7767	-0.7057	-2.8765
P	-0.3858	-4.2227	-0.8323
C	0.2716	-0.1359	-3.9889
C	2.1477	0.9835	-5.8219
C	0.1173	1.1618	-4.5179
C	1.4068	-0.8448	-4.4209
C	2.3294	-0.3049	-5.3205
C	1.0322	1.7171	-5.4134
H	3.1917	-0.8927	-5.6306
H	0.8703	2.7215	-5.8020
C	-2.3513	-0.4175	-3.2584
C	-5.0967	-0.0365	-3.9181
C	-3.3422	-0.2767	-2.2682
C	-2.7956	-0.3605	-4.5930
C	-4.1397	-0.1727	-4.9238
C	-4.6889	-0.0890	-2.5842
H	-4.4388	-0.1279	-5.9697
H	-5.4218	0.0204	-1.7865
C	1.2147	-4.8701	-0.2355
C	-1.6729	-4.7420	0.3553
H	-1.3415	-7.1319	-4.8546
H	-1.5634	-5.1044	-6.2578
C	0.3608	2.4860	1.2416
C	0.6568	2.3200	2.5733
C	0.9891	3.5738	3.2671
C	1.5870	6.1336	4.2956

(Table S6 continued)

C	1.3305	3.7303	4.6135
C	0.9594	4.7392	2.4507
C	1.2490	6.0043	2.9423
C	1.6258	5.0025	5.1132
H	1.3707	2.8597	5.2581
H	1.2215	6.8819	2.3003
H	1.8933	5.1121	6.1610
H	1.8210	7.1123	4.7042
B	0.6797	0.7047	2.9135
P	0.5147	4.1938	0.7896
C	2.2362	0.3382	3.2999
C	4.9656	-0.1602	3.9514
C	3.2203	0.1657	2.3072
C	2.6795	0.2509	4.6329
C	4.0158	0.0053	4.9594
C	4.5586	-0.0786	2.6185
H	4.3145	-0.0605	6.0043
H	5.2859	-0.2083	1.8185
C	-0.4076	0.2288	4.0327
C	-2.3632	-0.7148	5.8847
C	-0.3452	-1.0631	4.5930
C	-1.4925	1.0246	4.4429
C	-2.4531	0.5709	5.3508
C	-1.2988	-1.5322	5.4980
H	-3.2737	1.2245	5.6416
H	-1.2076	-2.5363	5.9095

C	1.8317	4.5367	-0.4294
C	-1.0173	4.9841	0.1852
H	-1.8138	4.8103	0.9133
H	-0.8705	6.0606	0.0536
H	-1.3070	4.5383	-0.7712
H	2.7712	4.1237	-0.0528
H	1.9433	5.6138	-0.5895
H	1.5861	4.0494	-1.3781
H	6.0069	-0.3542	4.1999
H	2.9272	0.2175	1.2606
H	1.9565	0.3598	5.4390
H	-3.1058	-1.0722	6.5945
H	0.4858	-1.7130	4.3236
H	-1.5956	2.0305	4.0385
H	-6.1443	0.1144	-4.1697
H	-3.0489	-0.3059	-1.2209
H	-2.0669	-0.4438	-5.3972
H	-0.7569	1.7446	-4.2324
H	2.8605	1.4079	-6.5257
H	1.5807	-1.8501	-4.0414
H	1.1758	-5.9584	-0.1255
H	1.4572	-4.4154	0.7297
H	1.9911	-4.6039	-0.9574
H	-2.6445	-4.4030	-0.0137
H	-1.6829	-5.8308	0.4663
H	-1.4812	-4.2777	1.3275

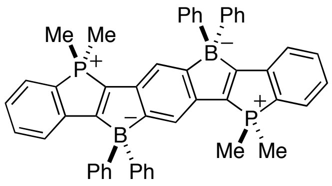
Table S7. Coordinates (Å) of the Optimized Structure for **10′** Calculated at the B3LYP/6-31G(d) level

atom	*x*	*y*	*z*
C	0.7724	4.6053	2.5857
C	1.1550	4.9554	5.3747
C	0.7953	3.5055	3.4893
C	0.9528	5.8766	3.1309
C	1.1387	6.0528	4.5080
C	0.9839	3.6674	4.8661
H	0.9498	6.7492	2.4805
H	1.2723	7.0547	4.9104
H	1.0005	2.8105	5.5403

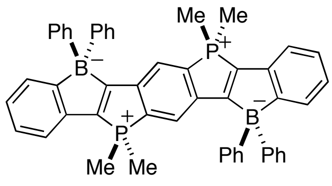
atom	*x*	*y*	*z*
H	1.3018	5.1052	6.4413
C	0.5886	2.2824	2.7207
C	0.4515	2.4851	1.3670
C	0.1775	1.2690	0.5997
C	-0.3016	-1.2681	-0.5723
C	-0.0410	1.1868	-0.7857
C	0.1301	0.0709	1.3606
C	-0.0970	-1.1840	0.8149
C	-0.2756	-0.0674	-1.3301

(Table S7 continued)

H	-0.0298	2.0934	-1.3816
H	-0.1145	-2.0896	1.4120
C	-0.5423	-2.4890	-1.3439
C	-0.7215	-2.2812	-2.6911
C	-0.8991	-3.5047	-3.4664
C	-1.1834	-6.0538	-4.4987
C	-1.1397	-3.6607	-4.8357
C	-0.7905	-4.6117	-2.5778
C	-0.9438	-5.8840	-3.1290
C	-1.2808	-4.9496	-5.3514
H	-1.2233	-2.7986	-5.4981
H	-0.8799	-6.7613	-2.4881
H	-1.4697	-5.0947	-6.4120
H	-1.2972	-7.0561	-4.9062
B	0.5463	4.0892	1.0367
B	-0.5191	-4.1010	-1.0351
P	0.4066	0.5536	3.0835
P	-0.5905	-0.5459	-3.0477
C	1.8048	4.4933	0.0767
C	3.9921	5.3008	-1.5631
C	1.9328	5.8132	-0.4013
C	2.8239	3.6004	-0.2993
C	3.8985	3.9878	-1.1051
C	3.0002	6.2157	-1.2035
H	4.6645	3.2619	-1.3726
H	3.0569	7.2448	-1.5530
C	-0.9098	4.5183	0.3980
C	-3.4739	5.0847	-0.7088
C	-2.0567	4.6480	1.2039
C	-1.1024	4.6883	-0.9861
C	-2.3568	4.9670	-1.5355
C	-3.3154	4.9261	0.6692
H	-2.4594	5.1052	-2.6110
H	-4.1754	5.0244	1.3294
C	-1.6897	-4.6051	-0.0162
C	-3.7462	-5.5842	1.6967
C	-1.6679	-5.9155	0.5025
C	-2.7884	-3.8111	0.3585
C	-3.7999	-4.2828	1.1998
C	-2.6715	-6.4016	1.3407
H	-4.6330	-3.6332	1.4633
H	-2.6141	-7.4201	1.7199
C	1.0026	-4.4232	-0.4872
C	3.6657	-4.7993	0.4670
C	2.1041	-4.5031	-1.3608
C	1.2940	-4.5441	0.8852
C	2.5958	-4.7294	1.3595
C	3.4095	-4.6878	-0.9012
H	2.7727	-4.8313	2.4294
H	4.2298	-4.7497	-1.6139
C	-2.1051	0.2484	-3.6889
C	0.7951	-0.0708	-4.1375
C	1.8825	-0.2646	3.7803
C	-1.0268	0.1144	4.1269
H	4.8243	5.6086	-2.1922
H	1.1645	6.5420	-0.1517
H	2.7854	2.5692	0.0475
H	-0.2426	4.6261	-1.6505
H	-1.9583	4.5370	2.2823
H	-4.4520	5.3073	-1.1297
H	2.0584	0.0918	4.7999
H	1.7464	-1.3506	3.7907
H	2.7475	-0.0147	3.1606
H	-1.1452	-0.9725	4.1781
H	-0.8846	0.5141	5.1355
H	-1.9263	0.5582	3.6919
H	0.4752	-4.5192	1.6023
H	4.6802	-4.9486	0.8293
H	1.9323	-4.4278	-2.4328
H	-2.8657	-2.7939	-0.0223
H	-4.5297	-5.9577	2.3524
H	-0.8328	-6.5675	0.2533
H	-2.9446	-0.0232	-3.0437
H	-1.9912	1.3370	-3.6957
H	-2.3075	-0.1045	-4.7048
H	0.8883	1.0186	-4.1847
H	0.6240	-0.4657	-5.1434
H	1.7189	-0.4983	-3.7391



8′



10′

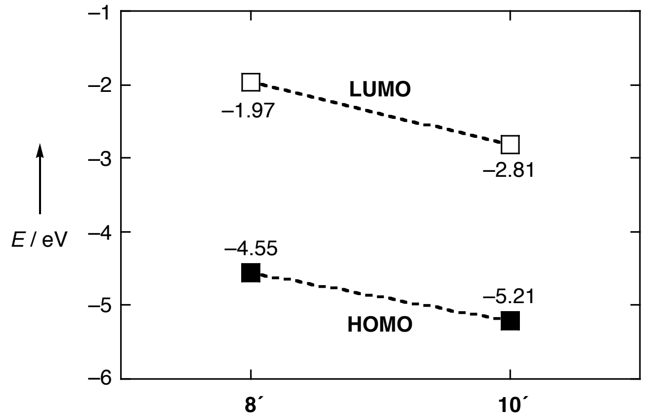


Figure S54. Comparison of electronic structures of **8′** and **10′** calculated at the B3LYP/6-31G(d) level.

Table S8. Lowest Excitation Energies of **8′** and **10′**[a]

cmpd	transition energy / eV (wavelength / nm)	main CI coefficient	oscillator strength *f*
8′	2.14 (578)	0.65534 (HOMO–LUMO)	0.3246
10′	1.92 (646)	0.66033 (HOMO–LUMO)	0.2051

[a] Calculated at the B3LYP/6-31G(d) level using TD-DFT method.

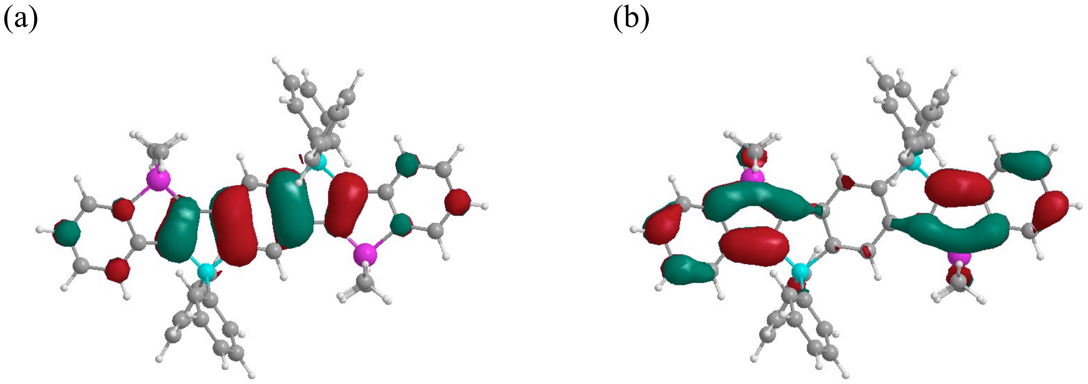


Figure S55. Pictroal representations of (a) HOMO and (b) LUMO of **8′** calculated at the B3LYP/6-31G(d) level.

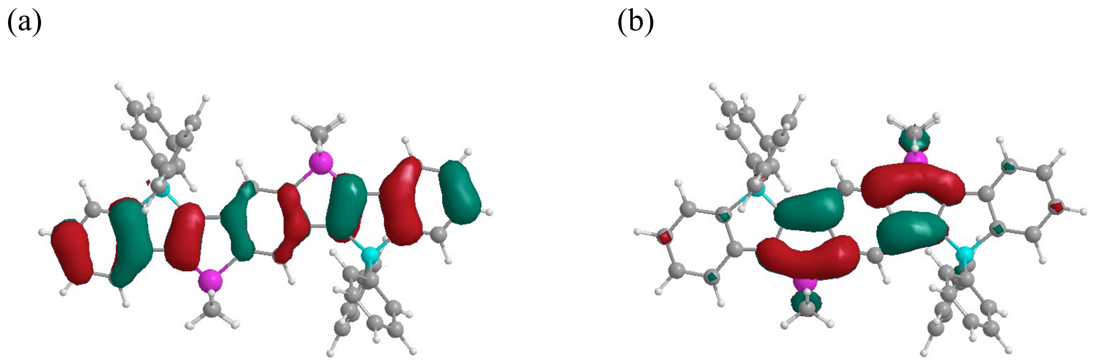


Figure S56. Pictroal representations of (a) HOMO and (b) LUMO of **10′** calculated at the B3LYP/6-31G(d) level.

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